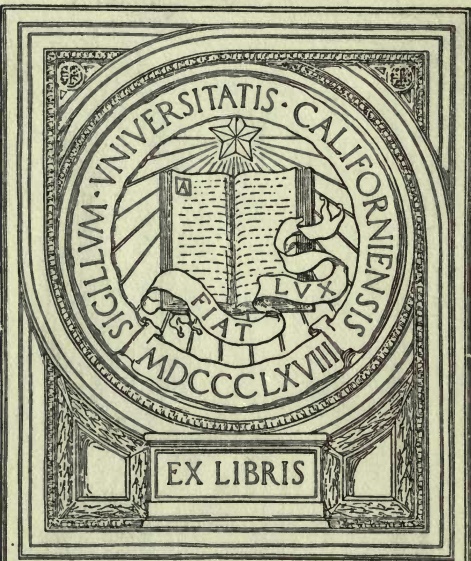


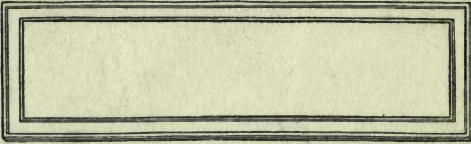
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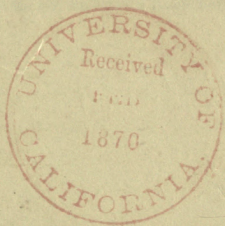








THE  
CHEMISTRY OF WINE.







THE

CHEMISTRY OF WINE.

BY

G. J. MULDER,

PROFESSOR OF CHEMISTRY IN THE UNIVERSITY OF UTRECHT.

EDITED BY

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LONDON :

JOHN CHURCHILL, NEW BURLINGTON STREET.

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LECTURER IN CHEMISTRY TO THE UNIVERSITY OF BIRMINGHAM

LONDON:

H. KEGONAS, M.D., F.R.S.

PRINTED BY SPENCER & CO., LTD.

LONDON:

JOHN BUNNELL, 27, BUNNELL STREET

PRINTED BY

## EDITOR'S PREFACE.

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PROFESSOR MULDER'S work on the Chemistry of Wine has been translated from the German edition. Dr. Oudemans has, at the Author's request, made many important corrections, of which the greater part have been inserted in the text, but an unfortunate delay obliges me to trouble the reader to correct some errors from the Table of Errata.

I have edited this work, because no English author has hitherto applied our present chemical knowledge to the study of wine, and neither at home nor abroad is there any one more competent than Professor Mulder to show the point we have reached, and to mark out the path to be pursued for the attainment of a perfect knowledge of the chemistry of wine.

HENRY BENICE JONES.

BROOK STREET,

*August, 1857.*

EDITORIAL ERRATA

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...of the history of wine

HENRY BAKER JOYCE

1877

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# O N W I N E.



## CHAPTER I.

### THE GRAPE.

THE quality of a particular vegetable is not unfrequently affected by external influences, so that it assumes a different character, which is distinctly imprinted upon the leaves or other parts, and may even to a certain extent be perpetuated. This property for the most part belongs to all organic bodies, and may be observed equally in the animal as in the vegetable kingdom. The dog is always a dog, but the Newfoundland and the lap dog, the sheep dog and the greyhound, differ from one another in no small degree. The cow is everywhere a cow, but differs in form in every part of the earth in which she is found.

Plants being still more dependent upon external influences than animals (which are restricted to no particular place), exhibit this peculiarity in a very high degree. The varieties of geranium, pelargonium, of the rose and dahlia, which belong nevertheless to one genus, are unlimited.

The difference is often impressed still more markedly upon the fruits which the plants produce.

There is, indeed, an identity in the nature of apple-trees; but any one, however ignorant of botany, can distinguish numerous varieties of this fruit, varieties not only of form and size, but also of colour, taste, and smell.

The vine ranks among those plants which are very dependent (at least in so far as regards the fruit it produces) upon external influences: colour and size, form and taste, aroma and productiveness, vary in this case in so remarkable a manner as might lead one almost to regard the vine as a peculiar gift of the Creator's bounty.

Should the reader wish for an example of the immense variety of vines, we will only remind him that Chaptal, when Minister of the Interior, caused 1400 different species of vines to be transplanted out of France alone into the garden of the Luxembourg.

The like variety may be observed not only in grapes which have been grown in different parts of the earth, but even in those produced in the same country, and growing on the same spot.

And, indeed, though less strongly marked, we may perceive a like difference even in the grapes of one vine. Protect one cluster of grapes from too great exposure to the action of the sun, and cover it with a bell of dark glass, or with oiled paper, while you leave another exposed, and you will produce a much more



finely-scented fruit in the former than in the latter.

It is not, therefore, strange that the grapes which grow on the sunny side of the Johannisberg should be very superior, as far as the flavour and fragrance of their juice is concerned, to those produced on the opposite side of the mountain; nor that, in general, a hotter and stronger wine is produced in warm regions than in such as are cold or temperate. If we add to this, that the peculiar nature of the soil, its constituents, the influx and drainage of water, the lightness or stiffness of the ground in which the roots spread; that further, the dryness or dampness of the air, and the change or equality of temperature, exercise a well-known influence upon plants and the fruits produced by them, we shall at least have a general idea of the varieties of the juice which constitutes the principal element in these berry-bearing fruits.

It is, moreover, sufficiently known that there is a general difference in the colour of grapes, between black, purple or red, and white; the juice of both is colourless, and colourless wine can therefore be obtained from both. If the black, purple or red grapes are pressed, and the skins thrown aside, a colourless wine, which in substance equals that procured from the juice of the white grape, is obtained by fermentation. I say substantially, for the variety in the juices, which even a slight difference in the external influences occasions, would effectually prevent the one

fermented liquid from equalling the other in flavour and aroma. Or is it, perhaps, that the heat of the sun penetrates more thoroughly the purple grape, while its dark skin partially preserves it from the action of light?

Is then the same chemical action possible to the juice of the purple grape (enclosed, as it were, in a small bladder) as that which is produced in the juice of the white grape by the difference between these two powerful influences, heat and light? We know that in our regions, the white grapes are much sweeter than the purple, and ascribe this peculiarity to the difference of the plants, but forget that in the easier passage of the light through the colourless skin of the white grape we possess a sufficient explanation of a more powerful chemical action, the result of which may be a larger formation of sugar. And if we generally find the purple grapes inferior in flavour and smell, we must ascribe this circumstance to heat, which in this case penetrates more easily the skin of the grape, and which in all living things is a powerful means of exciting chemical action. The principal component of the weight of the juice of ripe grapes is (in proportion to the weight) water, in which are various substances, either held in solution, or very minutely divided. As the juice is obtained by pressure, it is thick, and exposure to the heat of the sun changes it very quickly into a fermented liquor. As principal components we find in the juice sugar

(both grape sugar and fruit sugar), gelatine, or pectin; gum, fat, wax, vegetable albumen, vegetable gluten, and some other substances of the nature of extractive matters, which are not, however, accurately determined; tartaric acid quite free, and combined with potash, as cream of tartar, partly also combined with lime; in some cases we find also racemic acid, malic acid, partly quite free, partly combined with lime (Bérard), according to some, tartrate of potash and alumina; further, oxide of manganese and oxide of iron, sulphate of potash, common salt, phosphate of lime, magnesia, and silicic acid may also exist.

Up to this time no other ingredients have been discovered in the juice of the grape, but other materials must exist in it in small quantities, those, namely, which appear during fermentation, and impart to the fermented liquor, or at least tend essentially to produce not only the vinous smell common to all wine, but the aroma (bouquet), and the flavour respectively peculiar to each wine, in almost unlimited variety.

In cases where the skins are allowed, as in the preparation of red wine, to ferment with the juice, the elements which impart odour and flavour may be drawn from them.

But experience has not sufficiently decided even this point. What we know with certainty is, that colouring matter, as also tannic acid, may be extracted from the alcohol developed during the process of fermentation; colouring matter and tannic acid are,

therefore, equally formed in the skin, and dissolved in equal quantity in the wine; so that, in general, the more the red wines contain of colourless tannic acid, the darker they will be, that is, the more do they hold in solution of the colouring matter of the purple skins.

It is, therefore, possible to prepare lighter or darker coloured red wines, and to impart to them more or less tannic acid in proportion to the greater or smaller quantity of purple skins allowed to ferment with their juice.

As we shall have occasion hereafter to treat in detail of the colouring matters and of the tannic acid, we will only mention here, that the first are always simple; it is a blue matter, which, by means of the free acids of the wine, acquires a peculiar reddish colour. What other matters can be extracted from the skins, when these are allowed to ferment with the juice, is not known, but it is certain that the tannic acid in wine is derived principally from the skin; so that such wines as are prepared from fermented juice alone, without any admixture of skins, contain either none, or at best only a doubtful trace of its presence.

If the skins are allowed to ferment, the grape stones will not be excluded from fermentation, for in general one may take it for granted that an incomplete filtration of the expressed fluid will allow a large number of grape stones, richly provided with tannic acid, to ferment with it.

In those cases, therefore, where the fruit is allowed, after pressure, to ferment with skins, stones, and juice; or where the grape stones in larger or smaller quantities are included in the fermentation, a certain quantity of tannic acid may be obtained from them, although the amount, owing to the hardness of the covering of the seeds, will be but small. The same holds good with respect to the stalks of the grapes, which contain a good deal of tannic acid, and are often allowed to ferment.

Looking at wine, then, from a chemical point of view, the vine, with all its constituents, deserves our consideration in the first place.

The organic components of the wood are the common ones. Science is not, and perhaps never will be, in a position to bring the structure of plants into connexion with the nature of their products. But what it can do, and in modern times has earnestly endeavoured to achieve, is to investigate the organic constituents, and the relation between the necessary ingredients of the soil, and the nature of its vegetable products.

All wines contain cream of tartar, a salt which consists of tartaric acid and potash. The quantity and quality of the grape juice is connected, therefore, with the existence or non-existence of potash in the ground. Potash preponderates in the whole plant, and in all its parts, in the leaves and fruits, and also in the stem and boughs. If, therefore, a sufficient

quantity of potash does not exist in the soil, in addition to those other ingredients, which are equally necessary, the vine will not flourish. Further, with respect to the nature of the soil, the components of the ash, which are necessary to a successful development of the plant, must be found in it in sufficient quantity. The first condition necessary to the obtaining of good grapes is, that the plant should be well developed.

We need not, however, confine ourselves to this general direction, but can point out, with great accuracy, in many isolated cases, the important services which the incombustible constituents render.

With respect to the wine, we may observe, first, that certain of its peculiar properties, both of colour and taste, are connected with the quantity of the potash, soda, lime, magnesia, iron, manganese, sulphuric acid, phosphoric acid, and chlorine, which exist in it in larger or smaller proportions. The different proportions of these inorganic matters exert a very great influence upon the quality of the wine. If, for example, a good deal of phosphoric acid is contained in the grape juice, and a smaller proportion of lime, during the fermentation of the juice, a good deal of lime and magnesia (the latter as phosphate of ammonia and magnesia) will be thrown off.

The sulphuric acid and the chlorine are not withdrawn, they combine with potash and soda, with potash, which formed part of the cream of tartar in the grape juice. The tartaric acid then appears in

the wine, which did not exist as free in the grape juice; or, to speak accurately, more free tartaric acid exists in the wine than was present in the grape juice. The wine acquires a harsh or sour taste, and if it be red wine the colour is brighter, and many other properties are developed, which we shall have occasion hereafter to mention more particularly. All this is merely the result of the grape juice containing more phosphoric acid. And in like manner a larger proportion of lime or soda will cause other changes.

In order to explain the numberless varieties which exist among wines, it is necessary not only to take into consideration the so-called ash constituents, but to begin with the composition of the soil, and follow it through the different parts of the vine into the juice, and then pursue it afresh through the process of fermentation till the wine reaches us at table.

I need not apologize for giving in this treatise only a general sketch of the influence which these important materials exercise on the existence and growth of the plant, the development of the grape, and the formation of the wine. The quality of the soil may differ considerably without having a decided influence on the quality of the wine. Payen\* maintains that wine of very good quality, but of dissimilar bouquet, may be obtained from very different soils. The best Burgundy comes from a clayey lime soil; Champagne from a more thorough lime soil; Her-

\* Précis de Chim. Indust. 1849, p. 384.

mitage from a granite; and Châteauneuf from a sandy soil. A slaty soil produces Vin de la Gaude; a sandy one Grâves and Médoc, and a slaty one the wine of Lamalgue, near Toulon.\*

This variety of soil might lead one to imagine that all soils are equally suited to the cultivation of the vine. Such, however, is not the case; but as it is possible on the one hand that the principal constituents may be the same in apparently different soils, so, on the other hand, by the addition of vegetable matters, the difference of the soil may be adjusted or compensated. Inorganic vine manures are as important to the plant as the soil itself. The organic manure is also of consequence to the plant; if it is very nourishing, a larger quantity of wine will be produced, but the wine will not be so well scented nor so well tasted.

It is remarkable that fetid manures, such as fecal matters and the mud of great towns, exercise a very prejudicial influence on the odour of the wine, while, on the contrary, manures which are inodorous and putrefy slowly, such as wool, horn, and bone black, conduce very much to its fragrance. The putrefying

\* According to Peretti, iron and copper are found in the wine produced near Rome. (*Journ. de Ch. Méd.* 1832, p. 92.) Peretti has convinced himself that these metals were not admitted during the preparation of the wine. He evaporates the wine, burns the residue, and extracts the ashes by means of nitric acid, in which the metals are held in solution. Iron is known to exist in wine, and is therefore not remarkable; but up to this time no one else has asserted the presence of copper.



organic substances of the manure pass in such large quantities into the plant, that they are observable in the fruit, as, for example, in the cauliflower of the Westland, the smell of the putrid fish which is used to manure it can be recognized.

The publication of these facts at a time when it is asserted that plants do not bear a single trace of the organic constituents of the soil, is not without danger, but I venture nevertheless to allege them. I venture also to maintain, that no wine-grower who prepares good wine would give his vines putrid manure, although it has become the fashion among scientific writers to copy from one another the assertion that plants take up from the earth only carbonic acid, water, and ammonia, and prepare from them all organic substances. The leaves of the vine, which contain a considerable quantity of alkali, constitute an excellent manure for the plant. At the vintage only the fruit is removed from the field, and the leaves fall to the ground, when their ashes necessarily compose the best manure for future vine leaves.

Only in this manner can the fact be explained, that the vine requires so little inorganic manure, and often contents itself with substances which it obtains principally from the weather-beaten rocks on whose slope it is planted.

The following analysis will give an idea of the inorganic constituents to be met with in the plant. We give them as examples, and without attempting

any comparison between them and the constituents of the soil, because these are seldom specified in the forms in which they are directly conveyed to the plant, that is, in a soluble state. When in a soil substances exist in such a state of combination that they only become fit for use by exposure to the air for some time, then such a soil will nourish the plant in the long run, but is not generally in a condition to do so without the assistance of inorganic manure. For the rest I feel myself more at liberty to pass over the chemical composition of the soil, because I have never yet found any mention of the chemical composition of the incombustible manure of the vine.

In the first place, I shall therefore dwell on the nature of the components of the ash of the wood.

The branches of vine have the following ash components in 100 parts:—I., according to Hruschauer; II., according to Crasso; III., according to Levi.\*

	I. STEYERMARK.	II. MEISSEN.	III. WORMS WEINSHEIM.
Potash.....	34.1..24.9..26.4	44.2..37.3	17.5..25.3
Soda .....	7.6.. 7.0.. 8.6	2.9.. 1.8	27.2.. 2.3
Magnesia .....	4.7.. 7.1.. 9.2	4.8.. 1.0	9.1.. 7.5
Lime .....	32.2..37.6..33.5	36.0..43.7	30.2..40.8
Phosphoric Acid ....	16.4 .19.6..16.9	7.0.. 9.6	5.3..18.9
Sulphuric Acid .....	2.7.. 2.4.. 2.4	1.8.. 3.5	2.0.. 2.9
Silicic Acid.....	1.5.. 0.6.. 2.5	1.2.. 0.7	1.6.. —
Oxide of Iron.....	0.2.. 0.2.. 0.2	0.5.. 0.7	4.2.. 1.5
Protoxideofmanganese	— — —	0.1.. —	— — —
Common Salt.....	0.8.. 0.6.. 0.4	1.4.. 1.6	3.0.. 0.9
Ash per cent. ....	2.5.. 2.2.. 2.3	3.7.. 2.8	2.8.. 2.7

The following results appear to me to deserve less confidence, like those obtained by Levi, because the proportion of soda is so large.

\* Ann. der Chemie u. Pharm. Bd. 54, s. 332, Bd. 62, s. 59, Bd. 50, s. 423.

## Walz found in vine branches,—

	DEIDESHEIM.			SPEYER.		
	Traminer.	Riessling.	Rulander.	Traminer.	Riessling.	Rulander.
Potash.....	38·6	27·4	29·0	38·9	29·9	26·1
Soda .....	18·2	12·0	26·2	18·1	24·7	13·0
Lime .....	21·7	19·4	9·8	21·9	11·3	19·7
Magnesia .....	0·6	7·7	1·2	0·9	0·5	8·7
Phosphate of iron	1·9	3·1	1·7	2·0	1·8	1·9
Phosphate of lime	13·8	26·3	27·5	13·5	26·2	25·0
Sulphate of lime	2·4	2·3	2·3	1·4	2·2	3·3
Common Salt....	0·7	0·04	0·2	1·2	0·3	0·1
Silicic acid .....	2·3	1·8	3·2	2·1	3·2	2·1
Ash per cent. ....	2·9	3·0	2·9	2·8	3·1	2·9

We see that in all these analyses, except the first, by Levi, and that by Walz (which we therefore hesitate to accept), potash predominates considerably, but we find also that soda exists in the vine, and may therefore expect to find this alkali equally in the grape juice.

We find also lime in large quantities, and such other constituents as are common to the plant, and accumulate in larger or smaller proportions in the fruit. The quantity of phosphoric acid is not inconsiderable.

Berthier\* has given us an analysis of the ash of the vine and its different parts, from which the great difference between the ash of the wood and of the

\* Ann. de Ch. et de Phys. 3 Série, tom. xxxiii. p. 249.

fruit, and between the different parts of the fruit may be deduced. The following results of the ash of entire fruits collected at Namur in 1850, and known under the name of Gamay, is of the greatest value to us.

Sulphate of Potash .....	5·0
Chloride of Potassium .....	2·7
Carbonated Alkali .....	44·4
Carbonate of Lime .....	10·5
Carbonate of Magnesia .....	12·5
Phosphate of Lime. . . . .	23·5
Silicic Acid .....	1·4

Berthier gives also a comparison of the ashes of the different parts of the fruit of the purple and white grapes in the neighbourhood of Paris; the white are chasselas, the purple pineau. In 1,000 parts grapes were—

	Chasselas.		Pineau.	
Fruit-stalks.....	42·	0·6	ashes.....	36· 0·6
Skins and stones ..	220·	1·1	„ .....	240· 1·1 „
Juice.....	738·	1·9	„ .....	724· 3·0 „

The particular components were—

	CHASSELAS.				PINEAU.			
	Stalks.	Skins and Stones.	Juice.	Total.	Stalks.	Skins and Stones.	Juice.	Total.
Alkaline Salts ..	20	60	100	180	20	60	154	234
Carbonate of Lime.	26	12	35	73	26	20	72	118
Carbonate of Magnesia ..	..	8	12	20				
Phosphate of Lime.	14	30	47	91	14	30	72	116
	60	110	194	364	60	110	298	468

Boussingault\* gives the amount of the incombustible components of the grape-juice in Alsace in the following manner:—

Potash .....	0·842
Lime.....	0·092
Magnesia .....	0·172
Sulphuric Acid .....	0·096
Chlorine .....	traces
Carbonic Acid .....	0·250
Phosphoric Acid .....	0·412
Silicic Acid .....	0·006

He finds that the vine in these districts absorbs in the course of the year the following quantities per hectare (about  $2\frac{1}{2}$  acres of cultivated land):—

Potash.....	16·42
Soda .....	0·15
Lime .....	12·49
Magnesia .....	3·24
Phosphoric Acid .....	7·23
Sulphuric Acid.....	1·93

In the same districts the ground is exhausted in the following proportions per hectare:—

	Alkali.	Phosphoric Acid.
Potatoes .....	63.....	14
Mangel Wurzel .....	90.....	12
Wheat with straw.....	27.....	19

According to this, the assertion that the vine requires more alkali than other plants, on account of the grapes alone, is erroneous, nor can any probable reason be alleged for maintaining that the removal of the grapes alone, while the constituents of ash

\* Ann. de Ch. et de Phys. 3 Série, tom. xxx. p. 369.

in the leaves are returned to the soil exhausts the alkaline contents of the earth more than it is exhausted by the removal of other plants.

Crasso has given us\* a more exact analysis of the different constituents of the vine.

We extract the following:—

1. Must from unripe purple grapes of the small Burgundy or black Clavners (Metzger).
2. Must from ripe purple grapes, small Burgundy, or black Clavners (Metzger).
3. Must from ditto, but from a different place.
4. Must from ripe white grapes, Schönfeilners, or green Sylvaners (Babo and Metzger).
5. Purple skins from No. 1.
6. White skins from No. 4.
7. Stones from No. 1.
8. Stones from No. 4—all in 100 parts.

We find the wood of No. 3 analysed in the second column (p. 13), the first analysis.

	1.	2.	3.	4.	5.	6.	7.	8.
Potash.....	66.33	65.04	71.85	62.74	41.65	46.89	27.89	29.45
Soda .....	0.33	0.42	1.20	2.66	2.13	1.62	—	—
Lime .....	5.20	3.37	3.39	5.11	20.31	21.73	32.18	35.57
Magnesia ....	3.27	4.74	3.97	3.95	6.02	4.45	8.53	8.51
Oxide of man- ganese .....	0.82	0.75	0.10	0.30	0.76	0.51	0.35	0.45
Iron.....	0.73	0.43	0.09	0.40	2.11	1.97	0.45	0.65
Sulphuric acid	—	5.54	3.65	4.89	3.48	3.88	2.40	2.61
	5.19	—	—	—	—	—	—	—
	0.74	1.03	0.47	0.70	0.49	0.71	0.27	0.35
Silica .....	1.99	2.10	1.19	2.18	3.46	2.57	0.95	1.27
Phosphoric acid	15.38	16.59	14.07	17.04	19.57	15.66	27.00	21.05

\* Ann. de Ch. et de Pharm. Bd. 62, s. 59, u. Bd. 57, s. 69.

It was probably a mistake which led Crasso in an earlier examination which he made of vine branches of one and two years standing, with respect to the ash constituents, to imagine that he found more lime than potash.\*

The tables above given are of importance, both as exhibiting the respective proportions of the component parts named, and also in connexion with the previous summary of the incombustible constituents of the vine. In the first place, we see what appears remarkable, that soda, which constitutes a large portion of the ashes of the wood, diminishes considerably in every part of the fruit, and is entirely wanting in the stones; whereas the potash plainly increases in quantity, though to a less degree, in the skins than in the juice, so that two-thirds of the ashes consist of potash.

In Nos. 2, 3, and 4, we have the analyses of the unfermented grape juice, and I wish to direct attention particularly to it. We find in it oxides of iron and manganese, which pass partially into the wine, also a large quantity of phosphoric acid, which belongs to the albuminous substances of the grape juice, silicic acid, sulphuric acid, chloride of lime, magnesia, and a small proportion of soda, and sodium, combined with chloride, as muriate of soda.

In the juice of the unripe grape, Nos. 1 and 2, and in the constituents of the ash, we perceive no remark-

\* Ann. Bd. 57, s. 67.



able difference. The fruit appears, therefore (and this agrees with Couverchel's experiments upon the ripening of fruits), during the latest period of development, to have an individual life, and to be comparatively independent of the plant.

But, if the composition of the soil is of considerable moment to the development of the plant, and consequently to the formation of good fruit, the temperature of the region in which the vine grows exercises a no less important influence upon it.

In districts where the summer is sufficiently long and warm, and the temperature during the whole year never sinks below a certain minimum, the vine produces nothing but ripe and well-flavoured grapes. But when the vine yields exuberantly, the quantity of wine depends entirely upon the temperature.

Boussingault has given us some valuable information with respect to the quantity of alcohol produced per hectare (two and a half acres) of vineyard, taking into consideration the temperature of the air during the summer and the whole period of culture.\*

The production of alcohol depends necessarily upon two substances, upon the quantity of sugar which is formed per hectare vineyard, and the quantity of albuminous matter afterwards produced, or if we may assume that a sufficiency of albumen is always to be found in grape juice, then it depends on the sugar alone.

\* Ann. de Ch. et de Phys. tom. lxiv. p. 176.

The following table applies to the Schmalzberge, near Lampertsloch, a property belonging to Boussingault, which yields wine of very variable quality.

	Average Temperature			Wine per Hectare in hectolitres, 22 gals.	Alcohol in Wine, in volume.	Alcohol produced per hectare in 22 gals.
	During culture.	Summer.	Begin. of Autumn.			
	C.°' F.°'	C.°' F.°'	C.°' F.°'			
1833	14 7, 58 4	17 3, 63 1	11 4, 52 5	34·00	5·0	1·70
1834	17 3, 63 1	20 3, 68 5	17 0, 62 6	45·06	11·2	5·05
1835	15 8, 60 4	19 5, 67 1	12 3, 54 1	68·27	8·1	5·53
1836	15 1, 59 1	21 5, 70 7	12 2, 53 9	59·40	7·1	4·22
1837	15 2, 59 3	18 7, 65 6	11 9, 53 4	20·14	7·7	1·55

In the year 1834, when the average temperature during the whole period was highest, the largest quantity of alcohol was produced; the reverse was the case in 1833 and 1837. The temperature at the end of the summer appears particularly to affect the the quality of the wine, and this opinion seems justified by the results of 1811. As a general rule, however, a good vintage with regard to quantity does not necessarily involve excellence of wine, for the most productive years are frequently those which yield bad wine. It appears, therefore, that quantity and quality are not more intimately connected in the chemistry of the plant than in other cases.

The ripening of the fruit by the action of the sun is of the greatest importance in order to secure good

wine. On this account vines are not allowed to grow high, but are kept down, sometimes as low as three feet. Any one may easily be convinced that the grapes will ripen and develop better the nearer they are to the ground. The reason is, that they are exposed to the rays of the sun reflected back from the ground, and that the process of ripening is carried on through the evenings and nights by the warmth which is exhaled from the earth.

Let no one imagine that the vines are kept short in order to obtain a greater quantity of grape juice; for in the beautiful vine districts of South France, where in many places the vines are allowed to grow to the height of two metres ( $6\frac{1}{2}$  feet), a great quantity of juice is secured, but the wine prepared from it is much worse than that obtained in the same region and from the same kind of grapes when the vines are kept shorter.\*

The kind of grape is another cause of the great variety existing among wines. We know that the influence exercised by the nature of the plant itself upon its productions, depends to a certain extent, if not entirely, upon the circumstances in which it is placed during growth. Apples and pears may serve as

\* On an average, they reckon in the vine districts of France, to the hectare ( $2\frac{1}{2}$  acres) of ground, in the region of Toulouse, 462 gallons, (21 hectolitres,) in that of Gaillac 352, (16,) and a yearly total of 979 million gallons, ( $44\frac{1}{2}$  million hectolitres;) while in all the German states the yearly consumption is given at  $58\frac{1}{2}$  million gallons, ( $2\frac{2}{3}$  millions of hectolitres.)

an example of this; a golden reinette planted in another soil and in another temperature will cease to bear golden pippins.

The quality as well as quantity of the wine is affected by each individual variety of the vine.

The following kinds of grapes are particularly used in France in the preparation of wine:—

Le pineau noir or noirien, which makes good Burgundy, and in other districts also produces good wine.

Le gamay, which yields abundantly, but wine of inferior quality. This grape is best cultivated on flat lands, where the noirien seldom produces good wine.

Both these kinds of grape produce red wine.

Le pineau gris, le gamay blanc, and le furmint, make white wine; in Hungary, Tokay is prepared from the last mentioned.

There are, however, vine districts where the different kinds are not kept separate, where the plants are consequently allowed to attain a considerable age; and when fresh are planted, those of a higher flavour are selected. These mixed sorts never, however, yield the best wine; only grapes of one and the same kind must be used in order to procure that. If, therefore, those who have planted various kinds of vines together wish to make good wine, they must take care, at the vintage, to keep each kind of grape separate.

This caution is especially necessary (to the production of a useful wine) if purple and white grapes have been planted together; for as the purple grapes admit

the heat of the sun more readily, they are generally ripe ten or twelve days earlier than the white, so that to avoid the possibility of having a bad, sour wine, it is necessary, at the vintage, to pick the purple grapes before the white ones. It was formerly supposed that, by transplantation into different districts, the excellence of the better kinds of vine would be preserved; and with respect to some very richly scented sorts, the opinion has, within certain limitations, been justified. If, however, the vine is removed from a warmer to a colder region, the saccharine contents, as a general rule, diminish, and increase, if it is brought from a colder to a warmer district. Temperature and soil together determine, to a very great extent, the kind of grape. To no other cause can the perpetuation of the innumerable varieties be ascribed. Other appearances, however, in the character of the wine itself, teach us, that the soil may be exhausted just as much by the vine as by any other plant. There are districts in France where very famous wines were formerly made, and where only very inferior kinds can now be produced.

For example, the wines of Orleans are now considered very inferior to those of Burgundy, whereas formerly the reverse was the case. It may be said the vine is an alkaline plant; give it potash enough, and the wine will be better. But this is not the case. Orleans yields wine enough—a proof that there is sufficient potash in the ground, and yet the wine is no longer so good as formerly.

But I will not refer this circumstance to chemistry alone, for taste may have undergone a change, and the very same kind of wine which was formerly esteemed, may now no longer appear palatable. Sufficient care may not have been taken always to plant good sorts of vines in those places which were once famous, or another method may be used in the preparation of wine. But who can rightly understand that which has passed?

Bouchardat has examined several kinds of Burgundy, with respect to their capacity for producing wine, and has ascertained that the following kinds of grapes yield such and such quantities per hectare :\*

Kinds of Grapes.	Wine per hectare in hectolitres, (22 gallons.)	Alcohol hectolitres, (22 gallons.)	* Tartaric acid, Malic acid, kilogrammes, (2, 2 pounds.)	Potash, kilogrammes, (2, 2 pounds.)
Gamais blanc . . . .	240	7·88	112·4	15·3
Gros Gamais, (bad kind) . . . . .	160	8·18	67·2	9·44
Gros Verreau . . . .	90	6·28	36·9	5·13
Petit . . . . .	60	4·92	20·4	3·92
Melon . . . . .	80	7·28	24·3	3·92
Servoyen Vert. . . . .	50	4·40	17·0	2·35
„ Rose . . . . .	30	3·00	7·7	1·23
Pineau noir . . . . .	20	2·12	4·2	0·74
„ blanc . . . . .	15	1·52	3·9	0·61

\* Liebig and Kopp, Jahresber, 1847, 1848, § 1109.

Whilst he acknowledges that the plan of cultivation exercises an important influence on the wine, he is of opinion that it is more particularly affected by the kind of grape. And this inference may also be deduced from Bouchardat's remarks. These results are particularly worthy of observation, from the fact made evident by them, that the quantity of alcohol absorbed in the wine, produced yearly per hectare of ground, is not uniform with the production of potash or tartaric acid. A great deal more potash accumulates in one kind of grape than in another, though the quantity of tartaric acid or of alcohol will be proportionably less. As, however, we cannot here point out the chemical connexion between cause and effect, we will not linger over it, but limit ourselves to a full statement respecting the fruit yielding the juice which is to form the subject of our particular attention.

We have, therefore, to take into special consideration the grape juice, skins, stones and stalks, all four being of greater or less importance to the formation of wine. We must confine ourselves almost entirely, however, to the study of that which will give us a better knowledge of wine, and take it for granted that the rest is already known.

Among the constituents of the ash of the grape-juice we have particularly to mention alumina, it having been stated by many to exist both in grape juice and in wine.

The first who indicated the presence of alumina in

wine was Bischof.\* He discovered it in Rhine and Moselle wine when precipitated with ammonia; that phosphate of lime and phosphate of ammonia and magnesia were also mixed with it, is of course understood.

Alumina was formerly believed to exist in many vegetables, but this supposition has been proved to be erroneous, and it appears to be found really in very few plants. It would certainly be very remarkable did it really exist in grape juice.

Winkler, some years since, gave us the explanation of this remarkable phenomenon. When he had the grapes washed in pure water, and afterwards pressed, the alumina was to be found in the juice. Its origin is, therefore, not the plant, but the dust which sticks to the fruit, and adhering to the juice during the process of pressing, is afterwards (in so far as it contains soluble alumina,) taken up by it.

Alumina may therefore actually exist in wine, but is not to be regarded as a constituent of the plant.

Gunning burnt 31·85 raisins and obtained 0·3 ashes, which taken in conjunction with the stones and skins, gives 0·94 per cent. These were treated with hydrochloric acid, and the liquid thus obtained was warmed and filtered with a considerable quantity of liquid potash; to this clearer liquid hydrochloric acid, and after that ammonia were added. A slight thickness ensued, which, however, manifested no trace of alumina, and a little phosphate of lime was dissolved, as

\* Die vulcanischen Mineralquellen Deutschlands, s. 61.



was shown by the presence of molybdic acid, and oxalate of ammonia. There was no evidence, therefore, of alumina.

Is it not probable that were careful examinations oftener made, the same result would be oftener arrived at with respect to alumina in wine?

There is nothing particular to mention with respect to the other inorganic components of the fruit in connexion with the formation of wine, for, as they may all be referred to the usual constituents of ashes, there is no occasion to add anything to what has been already stated.

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#### THE ACIDS.

In considering the organic constituents of grape juice, we must devote our attention, in the first instance, to the acids found in it. These acids are differently specified. No one doubts the existence of tartaric acid, but there has been some uncertainty respecting citric and malic acid. The reason of this uncertainty is, that it is not possible to make such a general examination as would be necessary in order to obtain a positive result, since what does not exist in one kind of grape may yet be detected in another. And is any one able to analyse all the different kinds of grapes used for wine?

Schwartz\* discovered a considerable portion of

\* Ann der Ch. et Pharm. Bd. 84, s. 83.

malic acid in the juice of unripe grapes, and since then it has been several times subjected to examination. Proust considered the acid of the unripe grapes to be citric, and Kaufmann\* has stated that unripe grapes are peculiarly adapted to the preparation of citric acid.

Geiger† examined this subject more closely, and found in unripe grapes both tartaric and malic, but no citric acid.

This is all that we have found asserted with any probability respecting the existence of tartaric, and the existence or non-existence of citric acid. So far as we know, however, the three acids are rarely found together in one fruit, but either citric or malic, or tartaric and citric, or tartaric and malic acid. It would, therefore, be an exception to the rule, if all three were found in the grape juice in sufficient quantities to allow of their being accurately distinguished.

As, now, the existence of citric acid is not sufficiently proved, and on the contrary, the presence of malic acid in unripe, and of tartaric acid in ripe grapes is established, we may certainly assume that besides tartaric acid a fixed quantity of malic acid may be found in wine, which will be small in proportion to the ripeness of the grapes. No malic acid appears to exist in wine which has been prepared from perfectly ripe grapes. In some Bordeaux which

\* *Répert. der Pharm.* Bd. 14, s. 77.

† *Mag. für Pharm.* Bd. 7, s. 165.

we examined, a trace of malic, but no citric acid was found.

Winkler thought he had discovered an acid in the juice of unripe grapes, which he calls "para-citric." But Pasteur\* looked upon this as malic acid.

Until a few years since the opinion was entertained that in the grapes of the Vosges, and exceptionally in a few other kinds, an acid existed, having the same constituents as tartaric acid, but differing from it in its properties. Pasteur, Kestner, and others, have asserted that this, which is called racemic acid, is not so very rare. The last-named found it in insignificant quantities in 1850, in French and Tuscan wine; by the former it was detected in the tartar of many German wines. Pasteur succeeded in turning tartaric into racemic acid, by warming tartrate of cinchonine, or tartaric ether; in either case the result is the conversion of tartaric into racemic acid.

Considering how nearly related acids are to each other, and how possible it is to turn one acid into another, it can astonish no one that racemic acid should be more and more frequently met with in wine.

The admixture of a small quantity of racemic acid makes no difference whatever in the quality of the wine. And the quality of the wine is only affected by the presence of a large quantity of racemic acid, first, because less lime will then be found in it

\* Journ. de Pharm. 3 Série, t. xxiv. p. 75.

(racemate of lime being less soluble than tartrate of lime); and next, because cream of tartar is much more easily soluble in water than double racemate of potassa; the first salt being soluble at  $19^{\circ}$ , ( $66^{\circ} 2' F.$ ) in 204 parts water, the latter in 180 parts.

Wines, therefore, which contain, besides tartaric acid, a larger proportion of racemic acid, in consequence of the presence of this acid deposit during fermentation, (supposing an equal quantity of bases,) a larger amount of lime salt and potash. They are, therefore, sweeter, and if red wines, darker coloured than wines which contain only tartaric acid. At the same time this result depends entirely on the quantity of bases present at one time, for if these are less in wines containing racemic than in those in which tartaric acid is found, more free acid may be dissolved in the former, and the wine will then be redder coloured, and less sweet tasted.

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#### THE SUGAR.

The sugar which exists in grapes is called "grape sugar," although this name no longer denotes a particular kind of sugar. By a process to be mentioned hereafter, from 4 parts sugar from grape juice, only 3 parts can be obtained solid, and 1 part as fruit sugar. The grape juice is boiled with chalk, in order to saturate the free acids, the liquid is filtered, and the precipitate washed. The liquid matters are mixed

with albumen, boiled, filtered, and evaporated. After some time crystals of grape sugar are deposited, and new ones may be produced from the sediment by means of repeated evaporation.

As much as 40 per cent. solid particles, mostly of sugar, may be contained in the juice of very ripe grapes, but the greater number contain much less.

According to Chaptal, the grape juice of Touraine and the banks of the Cher and Loire has a specific weight of 1·0627—1·0825; according to Fontenelle, in 1822, it contained from 1·1029 to 1·1283.\* Reuss states it to be, in the environs of Stuttgard, 1·066—1·099. Günzler, writing of Marbach, in 1809, gives it as from 1·054—1·047; and in 1811, from 1·084—1·074. According to Schübler, in the Neckar district, 1·050—1·090; and according to Metzger, in the environs of Heidelberg, 1·039—1·091.†

Although this statement of specific gravities does not express the saccharine contents of the grape juice with accuracy, we accept it as a foundation, because by it we approximate to the truth. From it we deduce the following results:—

According to Chaptal, grape juice produced on the banks of the Cher and Loire contains 20—15 per cent. sugar; according to Fontenelle, 30—18 per cent. is contained in the juice produced in the South of

\* Dingler, Pol. Journ. Bd. 12, s. 337.

† Poggendorf's Ann. Bd. 42, s. 460; Dingler, Pol. Journ. Bd. 75, s. 139; Erdmann's Journ. Bd. 1, s. 358.

France. In the neighbourhood of Stuttgard, Günzler finds from 22—15 per cent.

In the grape juice of the same districts, Reuss, 25—13 per cent.

Schübler and Köhler, 24—14 per cent.

Hlubeck, in Styria, 26—17.

Metzger, in Heidelberg, 22—14.

Balling, in Bohemia, 23—14.

The extreme products are, therefore, 30—13. The increase of saccharine matter renders the formation of a larger amount of alcohol possible, but this depends partially upon other circumstances, which we shall treat of hereafter.

Only a very small quantity of sugar is contained in the grapes of this country (Holland), though they may, as we know, be used for wine; for an extract of the juice of fine purple grapes, dried in a temperature of 110° C., 230° F., produced only from 10 to 12 per cent. When one takes into account, however, the low and variable temperature of the autumn, it can be no matter of surprise that the preparation of wine in Holland should be very unsatisfactory.

## THE ALBUMINOUS SUBSTANCES.

We are acquainted with but few good analyses of the albuminous bodies found in grapes. Sometimes albumen, sometimes gluten, and sometimes both are spoken of. Beltz is the only person who has ventured to determine the quantities of these ingredients, and how he ascertained them remains a question. Beltz\* analysed the must of the Riessling grapes of Grumbach, and found in a quart, the specific gravity of which was 1·08—

Sugar .....	1680·6
Tartaric acid .....	7·7
Gluten .....	50·5
Cream of tartar .....	18·5
Alumina.....	3·0
Lime .....	2·0
Magnesia .....	2·0
	1764·3

According to this table, gluten and no albumen is found in the plant, hence there is about one-thirtieth of gluten to the quantity of sugar, and this, reckoning that from 13 to 30 per cent. sugar exists in grape juice, would give from 1 to  $\frac{1}{2}$  per cent. gluten.

Thénard appears to have detected gluten in the juice of the Johannisberg grapes; at least he found in it a sticky albuminous body, which, when exposed to the action of heat, presented all the appearances of

\* Jahrb. für pr. Pharm. Bd 14, s. 327.

albuminous matter. But even Thénard's examination cannot be regarded as conclusive and decisive, particularly as he asserts that this matter is soluble in boiling water.

It is, however, very necessary to know what albuminous matter is found in grape juice, in order to understand rightly the mode in which the ferment is produced in the juice.

The existence of this matter has been ascertained in the following manner:—

First, we must distinguish between the albumen found in the juice, and that which exists perhaps in the walls of the cells of the pulp, in the walls of those cells in which the juice is enclosed. These crushed cell-walls ferment with the juice, and exercise an important influence upon the fermentation.

The pulp of white grapes was freed from stones and skins, finely strained, and the juice then passed through filter paper. The pulp was rubbed and treated with water, until nothing but pure water passed through. The remaining cell-walls, after being warmed with potash, and strained, yielded, on addition of acid, pectic acid, as a product of the decomposition of pectose. The residuum was cellulose. The principal ingredients of the cell-walls seem to be pectose and cellulose.

A part of these cell-walls was boiled with acetic acid, the liquor so obtained was neutralized with ammonia after filtration. A white flocculent preci-



pitrate of albumen was obtained. By determining the quantity of nitrogen, the quantity of albumen was found.

0.316 of cell-walls, dried at 110° C. 235° F. gave M. Vlaanderen 0.048 platinum, or 0.007 nitrogen. Hence these cell-walls contain, in 100 parts, 14 parts albumen, if we reckon 15.5 per cent. nitrogen in albumen.

The cell-walls of the pulp cells of purple grapes consist therefore of

Cellulose	} .....	86
Pectose		
Vegetable albumen.....	.....	14
		100

This is a considerable quantity of albuminous matter. That this was really vegetable albumen and not vegetable gluten was proved by the treatment of the cell-walls with boiling alcohol. After filtering, on the addition of water, and evaporation, no vegetable gluten was precipitated. The existence of vegetable albumen in the walls of the pulp cells, which ferment in the juice, is of the greatest importance in the fermentation, for which reason we shall recur to it again at a later period.

With respect to the grape juice, when cleared and treated with alcohol, it yielded only a small deposit, white and flocculent, and mixed with a crystalline precipitate of the salts. This flocculent precipitate might contain either pectose or gum, but neither

vegetable albumen nor vegetable gluten; too little was obtained even from a large quantity of juice to allow of a satisfactory analysis.

The action of heat applied to the juice does not cause vegetable albumen to coagulate, for free tartaric acid retards the coagulation of albumen; acetic acid, potash, &c., have the same effect. The same cause prevents grape juice from becoming turbid by boiling. Grape juice evaporated to the consistency of an extract, and mixed with alcohol, gave no insoluble albuminous precipitate, for tartaric acid renders albumen soluble even in boiling alcohol. And if this extract of grape juice be mixed with water and with sufficient carbonate of ammonia to saturate the tartaric acid, the alcohol only produces a deposit consisting principally of salts.

According to the method of Will and Varrentrapp, the two following results were obtained by M. Vlaanderen with respect to the quantity of nitrogen found in the residuum of clear filtered grape juice, dried at 230 F., 110 C. :—

a. 1.128 gave 0.031 platinum.

b. 1.150 gave 0.0295 platinum.

This gives a. 0.39 per cent., and b. 0.36 per cent. nitrogen.

If we take the mean proportion, or 0.375, and compare it with albumen or gluten, reckoning the nitrogen in the organic elements at 15.5 per cent., we get, albuminous substances in the extract of grape

juice, 2.42 per cent. The grape juice referred to was expressed from Dutch grapes, and left a residue of 10 per cent. after evaporation.

According to this, and reckoning all the nitrogen as albuminous matter, we do not get in this grape juice more than 0.242 per cent. albumen; but if we reckon 9 per cent. sugar to 10 per cent. extract, every 100 parts sugar would find 2.18 per cent. albuminous matter ready for fermentation, which is a great deal more than is required.

The following are the contents of the purple grapes of these districts:—

Albuminous matters .....	0.24
Sugar .....	} 9.76
Extractive matters .....	
Gum, &c. ....	
Organic and inorganic salts .....	
Water .....	90.00
	<hr/>
	100.00

The existence of vegetable gluten in the grape juice is placed beyond doubt by treating the evaporated juice with alcohol, by filtering, adding water, and distilling the alcohol; but it is not therefore proved that an albuminous body may not exist in another form. The vegetable gluten is obtained as white flakes in the manner related above: these flakes adhere together on evaporation, and possess the well-known properties of vegetable gluten.

## PECTOSE AND PECTIN.

One of the constituents of the cell-walls in which the juice is enclosed appears to be (as we have already seen, p. 34) an ingredient called pectose, which is insoluble in water. During the ripening of the fruit, another substance is formed from this pectose, which is soluble in water, and is called pectin.

According to Fremy, this pectin is obtained from grape juice by precipitating the lime with oxalic acid, the liquid thus procured is precipitated with alcohol dissolved in water, and again precipitated with alcohol till it is quite pure. It then presents a thread-like body, soluble in water, and capable of being precipitated by means of alcohol in the form of a jelly, that is, supposing a good deal of water to exist in it. The constant increase of alcohol during the transformation of grape juice into wine, precipitates this matter. It is never met with in wine; if it should be found in it, it can only be in the sediment obtained by means of basic acetate of lead; for this and not sugar of lead precipitates it.

No connexion has yet been established between this pectin and the development of ferment in the wine, indeed but little is known of the peculiar properties of pectin. Its composition may be designated by  $C^8 H^6 O^8$  although Fremy reckons it at eight times

as much. We will not, however, dispute about the formula, but only intimate that more oxygen exists in it than in sugar, cellulose or gum, or than is necessary to form water. Pectin is not necessary for fermentation, for yeast, which contains none, is sufficient to ensure good fermentation in sugar and water. As, however, pectin is found in all sweet fruit juices, and all these, except when prevented by particular circumstances, ferment easily and strongly, and as nothing has been ascertained with respect to the disappearance of pectin during fermentation; therefore attention must be directed to this point before studying fermentation, and the question must be asked, Does pectin assist in the formation of wine or not? and, if so, how?

We must leave those to answer this query who are able to watch the traces of alteration in pectin on the spot where wine is made.

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#### GUM, OR VEGETABLE MUCUS.

Among the substances found in grape juice, and particularly deserving of notice in connexion with the formation of ferment, is gum or vegetable mucus, it being unnecessary at present to make a distinction between them. Gum is  $C^{12} H^{10} O^{10}$ ; vegetable mucus,  $C^{14} H^{19} O^{19}$ . The mode of preparation of pectin which is given by Fremy, assumes that gum or vegetable mucus, being insoluble in alcohol, will be

found mixed with pectin. The existence of one of these bodies (gum or mucus) in grape juice cannot be doubted, although it is not mentioned in Beltz's imperfect analysis. Alcohol precipitates them with pectin, and if strong alcohol be added to the grape juice of our country (Holland), it will be seen that they are precipitated, though in small quantity.

It has not been ascertained that gum or vegetable mucus are the only matters forming the integuments of the ferment-cells, which consist of cellulose; but there is no doubt that where one of these bodies exists, a considerable portion of such integument is formed by it.

The quantity present will be considerably diminished as the grape juice changes into wine, and being insoluble in alcohol, what may be produced from cellulose in the formation of ferment, will mostly be precipitated by the development of alcohol in the grape juice. Nevertheless, further on we shall see that gum exists in wine.

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#### GRAPE-SKINS.

In the preparation of some wines, the skins and stones, and in many cases, the stalks too, are allowed to ferment. An acquaintance with all these is, therefore, important to a thorough knowledge of wine. As far as our present object is concerned, there are only

two points to be considered with respect to grape-skins,—the tannic acid which is found both in purple and white skins, and the colouring matter, which is only met with in the skins of the purple grapes.

Not the slightest trace of tannic acid is to be found in the juice of either kind of grape. When tannic acid is discovered in white wine, it proceeds from the skins, a larger or smaller quantity of which were included in the fermentation. And the same holds good with regard to red wine; for no more tannic acid can be detected in the juice of the purple than in that of the white grape.

Any one may convince himself both of the existence of tannic acid in the skins, and of the presence of a larger quantity of acid in the purple than in the white skins, by boiling them with water, and adding gelatine, or salt of oxide of iron. The larger the quantity of skins, and the more they are pressed in preparing wine, the greater will be the quantity of tannic acid in the wine. Tannic acid is soluble in alcohol and water.

The juice of white grapes allowed to ferment without the skins yields a wine almost entirely free from tannic acid. Wines prepared in this manner lose less of their colour by age than any others. White grape juice, on the contrary, in which the skins are allowed to ferment, gives a liqueur-wine which darkens with age.

We shall speak more particularly of this circum-

stance in treating of liqueur-wines. At present we will only observe, that raisins prepared from white grapes cease to be white, and become light brown, the reason being that atmospheric action has changed the tannic acid contained in the skins into apothema, a brown substance. It is not, however, by the process of drying that the skins acquire a brown colour, for if they are softened in water they do not regain their original hue, but remain brown.

If the raisin skins are well soaked first in water, and then in liquid ammonia, so as to remove all tannic acid, a quantity of apothema is obtained from the tannic acid as a brown substance dissolved in ammonia.

I may here observe, that the contents of white raisins are no longer as they were originally, "colourless," but (in consequence of a peculiar change in one of the ingredients of grape juice, called extractive matter) are transformed into a brown substance, and coloured brown.

We shall speak more particularly of this point in treating of the colour of liqueur-wines.

The other component of grape-skins is the colouring matter which exists in purple grapes, and is the only cause of the colour of red wine.

Colouring matter is obtained from grape-skins in the following manner: they are well washed in water, then soaked in water and acetic acid, precipitated with sugar of lead, the precipitate washed, suspended



in water, sulphuretted hydrogen gas conducted through it, the sulphide of lead filtered off, boiled with water, and treated with alcohol and acetic acid, the liquid then allowed to evaporate, and the residue freed from fat by means of ether.

By this process, the colouring matter of the purple grapes is obtained pure. As it is also found in red wine, we prefer treating of it in detail later. Colouring matter is more easily soluble in alcohol and tartaric acid than in tartaric acid and water, and it is therefore easily obtained from the skins by means of the juice, which contains tartaric acid, and during the process of fermentation, when the quantity of alcohol is continually on the increase.

The colouring matter is blue, and the action of acids makes it red. In unripe grapes, which are saturated with acid, it is consequently red, and the riper they grow, the more the diminution of the acid causes it to become blue. The less acid the grapes contain, the darker are the skins, and consequently the wine extracted from the juice and skins is darker also. The skins of very sweet grapes are often black.

A considerable quantity of white wax may be obtained from grape skins by means of boiling alcohol, but this is of no particular importance to the wine. The wax sinks when cold, and a still larger quantity can be precipitated from the alcohol by the addition of water.

## THE STONES.

The stones of grapes are remarkable as containing a considerable quantity both of tannic acid and of a fatty oil, the amount of which Roy reckons at five and a half million kilogrammes (1 kilo. = 2·2 pounds) yearly for France alone. Roy considers that this oil is as well suited for food as for burning.\* Bendor† of Coblenz tried various experiments with this oil. By subjecting grape-stones, en masse, to pressure, he obtained 4 $\frac{2}{3}$  per cent. oil, and convinced himself that the oil does not cover one-fifth of the expense of pressing. Zeimer ‡ also extracted this oil in large quantities. He obtained a greenish-yellow oil, disagreeable to smell and taste, almost insoluble in alcohol, possessing a specific gravity of 0·950, and capable of drying very quickly if combined with oxide of lead.

Grape-stones, extracted with warm water after pressure, yield a strong solution of tannic acid, which was not removed by the previous pressure. Linderberger recommends the stones themselves as colouring matter,

\* Journ. de Ch. Méd. Janv. 1846, p. 7.

† Verhandl. des Coblenzer Gew.-Vereins, 1836, s. 42.

‡ Correspondengbl. des Württemberg. Landwilsch. Vereins, 1835, Bd. 1. Hefl. 3, s. 273.

and they might be so employed. Others have suggested roasting them and using them instead of coffee.

If, after being treated with water they are extracted with ether, the fatty oil spoken of before is obtained from them.

If the stones are fermented with the juice, more or less of tannic acid and of this oil will be dissolved; and as fat is found in wine, the existence of this oil in the stones is of importance.

This oil, obtained by the pressure of grape-stones, and their treatment with ether, has a spicy smell, and is coloured green by the admixture of a little chlorophyl.

I have not been able to prepare enough of it to examine it thoroughly.

In every case in which the stones are allowed to ferment a portion of this oil passes into the wine. It is therefore much to be wished that an analysis of this oil in connexion with the fat acids of wine should be undertaken, particularly as it is still an open question whether or no the fat acids of wine originate in the fermentation of sugar or not. We shall speak more particularly upon this point in treating of the odoriferous ingredients of wine.

But fat is also to be met with in grape juice; for, if the juice be allowed to evaporate, and the sediment be treated with ether, a product of fat is obtained, although the actual quantity be insignificant.

In the same way the quantity of fat acids existing

in wine is by no means large, and, without asserting that they are yielded entirely by the fat found in the juice and stones, it appears to me that the quantity of fat existing in these is more than sufficient to produce the fat acids of wine.

This point is of special importance, because the fat acids play a principal part in wine, and those wines in which the skins and oleaginous stones have been allowed to ferment, contain as a rule more fatty oil than those obtained from grape juice alone.

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#### GRAPE-STALKS.

The stalks deserve our attention for a moment, since they, too, are allowed to ferment.

They, like the skins, and especially the stones, have a sharp astringent flavour.

If treated with water, the addition of a salt of oxide of iron indicates a considerable portion of tannic acid. The other ingredients are of no value to us as regards our special objects.

Tannic acid may therefore be obtained from the skins, stones, or stalks, but not from the juice itself.

## ON THE FERMENTATION OF GRAPE JUICE.

The excellence of the wine must depend in no small degree on the ripening of the grapes, and the care with which they are gathered and treated.

In countries in which the vintage begins everywhere on the same day, it cannot but be that a good deal of wine will be prepared from unripe grapes. For it cannot be supposed that grapes growing in sunny and warm places will ripen at the same time with those which are more exposed to cold.

The quality of much home-grown wine might doubtless be improved, were the vintage more carefully conducted. Those who know the care expended upon the better sorts of grapes (even in the pulling of them), know also that the excellence of the wine depends not only on climate, soil, and the kind of grape, but also on the fostering care bestowed by man upon the vines.

A really well-flavoured wine can only be obtained from ripe grapes, and such as are free from admixture with unripe or overripe grapes. Great care must be taken during the vintage to keep the decaying grapes from the ripe ones; for to pick them over again afterwards is simply impossible, at least in the case of ordinary wines, which are prepared in large quantities.

Thus the possibility of the future wine being spoiled

dates from the vintage. The grapes used for the better kinds of wine are picked over again afterwards.

When the grapes and stalks are all pressed and allowed to ferment together, it is generally necessary that the fruit should be ripe enough for the stalks to look brown, the hard green stalks would spoil the wine, though they are sometimes considered indispensable in order to increase the quantity of tannic acid.

It is much to be wished with respect to every kind of wine, in order to obtain uniform quality, that grapes enough should be gathered in one day to fill one or several vats of the same size with their juice. It is well known that the course of fermentation depends partly on the quantity of liquid set in fermentation at once, that fermentation is generally better and more equally developed in large than in small quantities, and that the wines most prized by the consumer cannot retain any constant properties. These are facts which we admit without bestowing any particular attention upon them.

Let me make here two observations. The strength and peculiarity of some wines may be explained by the treatment to which the grapes are subjected before pressing. Tokay wine, for instance, is prepared from grapes which have been allowed not only to get over-ripe, but to a certain extent to dry upon the vines; Vin de paille is obtained from grapes which have been allowed to dry in the sun. In both cases water is

evaporated, and the juice, being more concentrated, yields a stronger wine. This is the method of preparation which the ancients made use of in order to procure heavy wines, rich in alcoholic contents. They evaporated the fresh grape juice by exposure to moderate heat, and the juice afterwards yielded a stronger wine. When the grapes are allowed to dry on the vine, the wine is called *vin sec* (dry wine); when they are dried on straw, *vin de paille*, grapes; and when the juice has been evaporated by means of heat, *vin cotti*, or boiled wine.

We have already seen (p. 32) that the saccharine contents of the grapes amount to from 13 to 30 per cent. of the juice.

If we reckon all this as grape-sugar, and in a hydrated state =  $C^{12} H^{14} O^{14}$  equivalent = 198, then as alcohol is  $C^4 H^6 O^2$ , and therefore equivalent = 46, and two equivalents alcohol are formed from one equivalent grape sugar, then 198 parts grape sugar would give, supposing there to be no loss, and all the grape sugar to be converted into alcohol, 92 parts of alcohol.

198 grape sugar gives 92 alcohol, but for the sake of brevity we shall consider them as 2 and 1.

According to this the juice of French and German grapes gives, when analysed, as a maximum, from 7 to 15 per cent. of alcohol by weight.

But some of the sugar remains undissolved, and during fermentation more alcohol is evaporated than

water; therefore, for such grape juice, or rather for the wine to be produced from it, the alcoholic contents must be under 15 per cent. as maximum, and 7 per cent. as minimum.

The knowledge that 92 parts alcohol in wine presupposes 198 parts grape sugar in the juice, enables us to arrive pretty accurately at the saccharine contents originally contained in the grapes. For example, a port wine containing 16 per cent. (by weight) alcohol, if it has not been mixed with alcohol must have been produced from grape juice containing 34 per cent. grape sugar.

Sugar is found in all wine, though in certain kinds but little exists; while in Muscadel and others we have 9 per cent. alcohol by weight, and from 22 to 24 per cent. residue after evaporation, of which more than 20 per cent. is sugar. Let us suppose 20 per cent. sugar in the wine; 19 per cent. sugar is necessary to the production of 9 per cent. alcohol by weight. 39 per cent. sugar must have been contained in the grape juice before the formation of such a wine was possible. If, therefore, sugar or alcohol has not been purposely added, the composition of such wines leads us to conclude that they were prepared from dried grapes.

Few examples are needed to show how close the connexion is between the saccharine contents of the grape juice and the excellence of the wine to be prepared from it.



When the summer has been unfavourable, owing to want of heat and excess of rain, the grapes often yield juice which contains less sugar, but a considerable portion of acid, and albumen enough to cause fermentation, if only the necessary quantity of sugar were there.

The desire to obtain, notwithstanding, a serviceable wine, often leads at this stage to an attempt to introduce foreign elements into the juice, and to doctor it.

The simplest plan is to add sugar to the juice which is deficient in saccharine matter:—common cane, or beetroot sugar, or on account of its cheapness, potatoe-syrup (glucose) are added, and in sufficient quantities to compensate for the deficiency in the juice. So long as the sugar is pure, it matters little whether cane sugar or glucose be employed, since both yield alcohol.

The admixture with sugar cannot afterwards be detected; chemistry is here at fault, since only that which was wanting in the fruit has been added to it.

It is scarcely necessary to mention that wine with an aroma cannot be obtained in this manner from grapes which have ripened badly. Raisins are often used for the inferior German wines.

The same means, viz., the addition of sugar to grape juice, are often employed to obtain a stronger wine from good grape juice. In this manner many kinds of strong wine are made to imitate port wine.

Here, as well as when the juice is sour, much

depends on the presence of a sufficient quantity of the matter necessary to fermentation, and these are generally present, at least up to a certain point. Besides this, it is of consequence that the sour grape juice should not contain too much tartaric acid, for this is not entirely removed by the sugar, though rendered for the most part ineffective as far as taste is concerned.

In this case another remedy is employed, and we are obliged to call both this and the addition of sugar (with whatever intention it may be made) adulteration; for wine, in the sense in which alone we are now considering it, professes to be grape juice changed by fermentation, and nothing more nor less. The means used are these: chalk is added to a portion of freshly expressed juice (must), and its free acids are thus withdrawn; for example, the free tartaric acid existing in the juice, and half the cream of tartar. The portion of juice mixed with chalk is exposed to partial evaporation, allowed to cool, and the precipitate deposited. In this manner a juice is obtained which has been deprived by lime of all its free acids, has gained relatively by evaporation in sugar, and contains the so-called neutral tartrate of potass. Now if to this another portion of the original must be added, the free tartaric acid of the latter combines with the neutral tartrate of potass of the former, and forms a fresh cream of tartar. The whole thus becomes less acid, and its saccharine contents are increased by the

addition of that portion which has been exposed to evaporation.

It follows of course that, since the must necessarily loses by evaporation, the wine suffers diminution in quantity.

One or other of these adulterations may however be considered certain after an unfavourable summer.

Let us now pass to the consideration of the liquid as it flows from the wine-press.

Shortly after pressing, the liquid appears to be in motion, and little air bubbles rise to the surface; fermentation has begun; the juice, not quite clear at first, becomes more turbid, the motion of the liquid increases, and froth is formed on the surface; the gas bubbles become larger, the consistency of the liquid decreases, as do also its saccharine contents. In place of these more and more alcohol is engendered, and the liquid, originally watery, and now enriched with alcohol to a greater or less degree, can no longer retain in a state of perfect solution various matters which it previously held in that condition. Fermentation reaches its highest point with greater or less rapidity according to the temperature; in a moderate climate it generally occurs in from three to four days.

When the fermentation is diminishing, and before it is completely finished, the whole mass of liquid is stirred up, in order to bring its elements into contact with each other afresh. I know not whether the practice still exists; but till within a few years, in

many parts of France the infamous custom (for how else can I designate it?) prevailed of allowing a naked man to go into the wine-tub, who not only stirred up everything, but promoted fermentation by the temperature of his body, (37 C. 98 F.). According to Thénard, several individuals have been killed in this way, the atmosphere of carbonic acid in which they found themselves proving fatal to them.

After some days the whole mass reaches its highest point of effervescence, and at this it remains for three or four days; it then begins to diminish, and by forming a precipitate at the bottom allows the wine to become gradually clearer.

The wine is now removed into another vessel, the sediment being left behind. Fermentation continues, but more quietly; and this is called after-fermentation. Sugar is constantly being converted into alcohol and carbonic acid, and a fresh precipitate is continually forming and depositing itself at the bottom.

After the wine has undergone this after-fermentation for several months,—(and the fermentation generally increases again during the next spring, at the time it is said when the vines blossom, that is, when the warmth of the air excites fermentation again,)—and has been drawn off from time to time into other vessels, in order to free it from the sediment which has been continually forming, it is transferred into casks in which it can be exported. Five conditions are necessary to the fermentation of wine; the three

last of which, namely, 1. the presence of water, sugar, and an albuminous matter in a state of actual change; 2. warmth; and 3. the admission of atmospheric air, must be more particularly considered.

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#### ATMOSPHERIC AIR.

Many years ago an experiment was tried by Gay-Lussac, which appeared to prove that although air was essential to the promotion of fermentation, yet that only so much was required as might serve to initiate the process, which would then be continued and ended without it. He placed grapes upon quicksilver freed from all air bubbles, broke them with a metal wire, let them remain in this state quietly for some days, and then he saw no signs of fermentation. When he afterwards introduced a little air bubble, active fermentation was at once excited, and continued without interruption.

This experiment and the conclusion drawn from it have been interpreted in various ways. Not only have some asserted that no air was necessary to the development of fermentation; but exactly the opposite has been maintained, viz., that a free admission of air during fermentation improves the wine.

Döpping and Struve\* thought they had ascertained

\* Erdmann's Journ. Bd. 41, s. 275.

by experiment that fermentation might be completed in carbonic acid or hydrogen gas, without a trace of oxygen; but they never saw fermentation commence without it. That little or no air is necessary to the continuance of fermentation is certain, for it was the custom for many years in France, in order to prevent the loss of alcohol during fermentation, to cover the wine-coops with a cask lid, provided with a long pipe, wherein the alcoholic vapours were condensed.

In this manner the admission of air to the fermenting liquid was completely cut off, for both cask and pipe were speedily filled, and kept filled, with carbonic acid. But this apparatus has fallen into disuse since Gay-Lussac proved that when open vats were used, scarcely  $\frac{1}{200}$ th part of alcohol was lost in consequence. Neither before, during, nor after its use, was any change found in the quality of the wine; and yet such must have been the result, if a large quantity of air were necessary to the preparation of wine. After an account of the method of preparing Bavarian beer, where the air is allowed to enter freely, Liebig recommends the same in the case of wine, and suggests that a large opening should be made in the casks in which fermentation takes place. Von Babo, a vine-grower in Baden, "in accordance with this advice, allowed wine to ferment in casks provided with large openings."\*

This experiment was made in 1841, with red wine,

+ Liebig. Ch. Briefe, 1851, s, 302.

and was repeated at Johannisberg in 1846 with great success, Prince Metternich having placed 6 casks, each containing 1200 bottles, at the disposal of the experimenters. An aperture of six square inches, covered with a piece of coarse canvas, was sufficient.

The wine which fermented in them was of a better quality than that which underwent the same process in a cask which was closed and only provided with a glass tube for the passage of carbonic acid. Experiments of the same kind, tried by Crasso,\* were equally successful.

But in other experiments, made with white wine, the wine in open casks appeared to lose in aroma; doubtless, therefore, much depends on the kind of wine.

From these experiments we may, however, deduce the general principle, that wine placed in open casks requires a lower temperature, while for that put into closed vessels a greater degree of heat is necessary during fermentation. Wines containing a great deal of sugar may therefore be allowed, with advantage, to ferment in closed vessels, whilst those less rich in saccharine contents may be left in open casks, provided the temperature be low and equable.

Many, however, have opposed this opinion of Liebig, and Schubert † in particular attacked it, stating

\* Liebig's Ann. Bd. 59, s. 360.

† Erdmann's Journ. Bd. 36, s. 45.

that he, by the use of the same means, had obtained very unfavourable results; Liebig defended himself, and maintained that the experiments had been badly tried. Not having any practical experience in this matter, I cannot enter more particularly upon it. But something appears to me to have been overlooked.

The admission of a large quantity of air is not only unnecessary but injurious, if the object desired be to increase the quantity of alcohol. If wine of another quality is wished, this may be obtained by regulating the quantity of air admitted during fermentation. Every kind of grape juice cannot bear the admission of air in large quantities, or at least circumstances may occur, which may render it possible to obtain good wine, if the air be excluded.

These three conclusions are, if I do not mistake, generally admitted.

The last observation is so completely the result of large experience, that it appears unnecessary to dwell upon it longer. If any one should still maintain that every kind of grape juice can bear the admission of air in large quantities, we would only ask, Why, then, did experiments tried with grape juice in open vats fail, while the very same grape juice, placed in closed vessels, yielded good wine?

The two former results are deduced principally from experiments by which De Saussure\* tried, and proved that a large admission of air is unnecessary

\* *Bibl. Univ. t. xxxii. p. 168.*



and injurious to the production of a large quantity of alcohol.

375 grammes (5787·7 grains) of must were put into a flask from which air had been expelled, and a globe, capable of containing 44 litres ( $77\frac{1}{2}$  pints), out of which also the air had been pumped, was screwed upon it. Except, therefore, for the minimum quantity of air which the liquid might have absorbed during pressing, it might be looked upon as fermenting in a space devoid of air.

At the same time, an equal quantity of the same must was put into a bottle filled with air, and a globe filled with air was screwed upon it. This globe was, during the two following days, freed every now and then from the gaseous contents present in it, and furnished with fresh air. This liquid might, therefore, be regarded as possessing an excess of air.

At the end of four weeks the liquids were distilled, when the quantity of alcohol found in the flask devoid of air was four times as great as in that filled with air.

This result again intimates that much air is unnecessary, and even injurious to the production of alcohol. That it is unnecessary, was sufficiently proved by the large experience obtained from the fermentations in Gervais's apparatus (vats covered with loose lids), the object of which was to condense into water the alcohol escaping with carbonic acid; that it is injurious, is proved by the acids which a

large admission of air engenders from the wine. An experiment by De Saussure has proved this also.

The reaction of the must was acid before the experiment, so that 0.81 grammes (12.5 grains) of ammonia were necessary to saturate the acid in 375 grammes (5787.7 grains) of must. Now, after the experiment narrated above, it was necessary to add to the juice which had fermented without air, in order to neutralize its acidity, 0.76 grammes (11.7 grains) ammonia, but to that which had fermented in the air, from 5 to 6 grammes (77 to 92 grains), that is six times as much. The acid was acetic acid. That is to say, the freer admission of air caused the formation of acetic acid in the same proportion in which alcohol disappeared from the liquid.

The action of the oxygen in the air changes the alcohol into acetic acid.

Though on the large scale the result might be different, the experiment teaches sufficiently that but very little air is required for the preparation of wine. These inferences do not, however, render it impossible that under favourable circumstances certain kinds of grapes might produce a better flavoured wine, if during fermentation a certain portion of air were admitted. This is clear from the method used in the preparation of Bavarian beer, as opposed to that common among us. And it is my conviction that Liebig's opinion ought not to have been so severely attacked as it has been.

## TEMPERATURE.

Supposing, however, that soil, climate, the kind of grape, and many other circumstances have concurred, and done their best to produce good wine, the result may still be a failure, unless during the whole process of fermentation a sufficiently high temperature can be maintained.

There is a wide interval between the extremes of temperature in which fermentation is possible, but the boundary is very narrow which limits good and active fermentation in every kind of wine.

It is unnecessary here to mention the degrees, but how very various is the heat in autumn, during which time wine is prepared in different countries! An acquaintance with many details of which we are still ignorant is, however, necessary, in order to investigate thoroughly the influence of temperature upon a good, well-tasted wine, which should not spoil with age. The grapes of each country ripened under different degrees of summer warmth, and very unequally rich in constituents, require different temperatures during fermentation, and different temperatures are also required for grapes which are the product of a warmer or colder summer.

But we are still quite ignorant upon these points. All we know is, that a high temperature during

autumn promotes fermentation, and a low one is detrimental to it; that inequality of temperature during fermentation is extremely injurious, and not unfrequently spoils the wine altogether. It has further been ascertained that in consequence of the chemical action, and notwithstanding the escape of carbonic acid, the heat of the liquid exceeds that of the air.

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FERMENT.

Fermentation is a term used to express that chemical change, taking place in an organic substance, which is capable of being transferred to another organic body from which various products, some of them in the form of gases, can arise.

Grape and fruit sugar are the materials upon which the active forces in the fermentation of wine are brought to bear; both sugars have the same composition, and can be alike converted into alcohol and carbonic acid.

1. Equivalent Sugar . . .	$C^{12}$	$H^{12}$	$O^{12}$
2. „ Alcohol . .	$C^8$	$H^{12}$	$O^4$
4. „ Carbonic Acid	$C^4$	—	$O^8$

The substances from which the active force proceeds are albumen and vegetable gluten, which are both easily convertible, and which transfer the che-

mical change in their constituents to the constituents of the sugar. There is a fixed relation between the quantity of alcohol produced (a sufficiency of sugar being pre-supposed), and the quantity of albuminous matters capable of undergoing change which sets up fermentation. According to Thénard, 100 parts of sugar require  $1\frac{1}{2}$  parts ferment, reckoned in a dry state. The analysis of ferment teaches us that about half of it consists more or less of albuminous matters, and therefore  $\frac{3}{4}$  parts albumen are required in order to convert 100 parts sugar into alcohol and carbonic acid.

We must address ourselves more particularly to the examination of ferment, not only on account of its connexion with the preparation of wine, but also with regard to the constituents of wine.\*

I may here observe, in few words, that some years since an examination of ferment and fermentation enabled me to obtain some general results,† which agree with those given by Dumas,‡ Mitscherlich,§ and Schlossberger,|| in so far as they relate to this matter.

Ferment consists of cells, the substance of which

\* Fabroni, Bertholon, Le Gentil, Mourgues, Chaptal, Dandale, Parmentia, Gervais, Aster, Herpin, Colier, Fontenelle, and others, have written upon fermentation, and especially upon the fermentation of wine. The treatises of the two last named appear in the *Ann. de Ch. et de Phys.* tom. xxv. p. 133, and tom. xxviii. p. 128, and in the *Journ. de Pharm.* Sept. 1823, p. 437.

† Scheik. *Onderz.* deel. ii. p. 409.

‡ *Versuch einer Chemischen Statistik*, s. 88.

§ *Lehrbuch der Chemie*, 4 Aufl. s. 370.

|| *Liebig's Annalen*, Bd. 51, s. 193.

itself takes no part in the action; the contents of these cells are the matters which cause fermentation. Ferment belongs to the albuminous class of substances, and is everywhere produced from vegetable mucus.

The albuminous substance of the ferment may be extracted from it by means of strong acetic acid, and precipitated by carbonate of ammonia. Then after having been treated with alcohol, the contents of the cells are obtained free from ash, and of the following composition:—

C.	.	.	.	53·4
H.	.	.	.	7·0
N.	.	.	.	15·8
O. S.	.	.	.	23·8

Albumen and gluten have the same composition. The cell-walls consist of cellulose, and are produced from gum, or vegetable mucus.  $C^{12} H^{10} O^{10}$ .

Other bodies which belong to the order of albuminous substances, but are not enclosed in cells, may also, under certain modifications, cause sugar to ferment. If gum or vegetable mucus and air are present at the same time, ferment will be formed when fermentation occurs.

Fermentation, which means here the conversion of sugar into alcohol and carbonic acid, continues during the formation and decomposition of ferment. Fermentation is in the first instance the consequence of the conversion of albuminous matter, (be it vegetable

mucus, or vegetable albumen, or both,) into a body which is soluble in water, insoluble in alcohol, and contains far more oxygen than the substance out of which it is formed. This body may be procured from ferments either by boiling them, or simply washing them with cold water.

The quantity of oxygen found in this matter is to the oxygen in the substance out of which it is formed nearly as 3 : 2.

The formation of this matter is one of the chief causes of fermentation.\* As soon as sugar comes in contact with yeast, the albuminous contents of the ferment cells exude through the partitions of the ferment cells, absorb oxygen from the air, and transfer this chemical action directly to the sugar.

The transformation of the contents of the ferment cells into a body rich in oxygen, into which albumen and gluten may also pass, is not, however, the only change which occurs during fermentation, the transformation proceeds to the formation of ammonia.

The highly oxygenated substance, the formation of which sets up fermentation, is either decomposed or precipitated from the liquid by the alcohol which is subsequently formed; it is this body which is dissolved when ferment is treated with cold water. It is insoluble in alcohol.

\* The primary cause of the motion of the molecule is probably that the phosphorus of the albuminous group is oxydized, forming phosphoric acid.

Ferment cells are not necessary to fermentation, only their contents are requisite.

Vegetable gluten and vegetable albumen, with sugar and gum, or vegetable mucus, form when brought into contact in a sufficiently warm temperature, the new highly oxygenated matter, and engender ferment, and at the same time set up fermentation; two operations, the result of one cause.

The gum or vegetable mucus is thus changed into cellulose, and forms insoluble cells in water. The vegetable gluten, or albumen, is enclosed in the cells, and retains the chemical capability peculiar to it, of taking up oxygen.

On this account the globules of ferment are well adapted to the engendering of fermentation; their contents have only to exude through the walls of the cells in order to give the sugar an impulse to decomposition. It is however necessary that the action of vegetable acids should keep the ferment acid. Without absorption of oxygen the albuminous contents of the ferment cells, which are insoluble, cannot be changed into soluble bodies rich in oxygen, and thus become capable of further decomposition. Very little oxygen is, however, necessary, since two parts sugar scarcely require for fermentation three-fourth part of albuminous matter in a state of oxidation.

When the air, which has either been dissolved in the liquid or freely admitted to it, does not furnish



this oxygen, it seems that the sugar supplies it, and fusel oil, containing little oxygen, is the result. (See the Odoriferous Constituents of Wine.)

The soluble substance rich in oxygen formed from albuminous bodies, which for the sake of brevity we call extract of ferment, constitutes one-fourth of the substance which exists in the cells.\* This may undergo further transformation, and is capable of taking up more oxygen, and by so doing decomposes sugar; hence the substance extracted from ferment by cold water is capable of producing fermentation.

As this representation of the operation of ferment rests upon experiment, certain important examinations made by C. Schmidt are of great value to us in completing it.† He has proved that the change undergone by the albuminous contents of the ferment cells is not limited to the formation of a highly oxygenated matter soluble in water, and insoluble in alcohol, but that this matter when once formed is subject to further decomposition, in consequence of which ammonia is formed, and may be obtained from the liquid after fermentation by means of sulphate of magnesia and phosphate of soda, as phosphate of ammonia and magnesia. We must therefore assume that the albuminous contents of the ferment cells is a continually decomposing body, which during the process of decomposition furnishes ammonia and other by-pro-

\* Scheik. Onderz, deel. ii. p. 461.

† Ann. der Ch. und. Pharm. vol. lxi. p. 168.

ducts. A complete decomposition of this albuminous body into ammonia, carbonic acid and water is not to be looked for. We know nothing more certain of this, though we are well aware that albuminous matters readily yield ammonia, if, for example, they are gently warmed with an alkali.

Schmidt's experiments make us thoroughly acquainted with the decomposition. 5 c. c. of beer yeast left after being washed with water, as dry sediment, 0.410 (6.3 grains). Had it not been washed, a larger sediment would have been obtained, but it is sufficient for our purpose to know the result just mentioned. After this 5 c. c. of beer yeast had fermented with 3 grammes (46.3 grains) of sugar for eight days, 0.098 (1.51 grains) phosphate of ammonia and magnesia was obtained from it in the manner related above: in another experiment, in which urea was present (without, however, being decomposed) the result was 0.103 (1.59 grains). So that 0.012 (0.18 grains) nitrogen escaped from these quantities of yeast in the form of ammonia during the eight days' fermentation.

In the albuminous substance of the contents of the cells we find  $\frac{1}{2}$  5.8 per cent. nitrogen; so that we may fairly reckon in 0.410 (6.3 grains) yeast, more than half of which consists of albumen, 0.032 (0.49 grains) nitrogen.

In eight days 0.012 (0.18 grains) escaped. If, therefore, the albuminous substance was entirely freed

from nitrogen in the form of ammonia, it follows that one-eighth of the contents of the cells underwent complete decomposition. We cannot, however, consider it as certain that during fermentation the albuminous matter was completely resolved into ammonia, carbonic acid, and water. By the putrifying of caseine, leucine is formed, and the progress of the same process in other bodies gives rise to other nitrogenous substances.

An investigation which should follow out the results of the decomposition of ferment during the fermentation of sugar would be of the greatest value, especially with regard to wine, for as far as these matters are concerned, we are almost entirely ignorant.

I may here just notice one observation of Schmidt's. During fermentation, he found the ferment (considered to be dry) increased in weight, which can only be accounted for by the conversion of sugar into cellulose.

5 c. c. of beer ferment, washed with water and dried, gave a dry residue of 0.410 (6.3 grains); the same quantity of ferment, after fermenting during eight days with 3 grammes (46.3 grains) of sugar, gave a dry residue of 0.628 (9.7 grains). This last had yielded 0.012 (0.18 grains) nitrogen in the form of ammonia; it had lost in albuminous contents, and yet had gained in weight. The ferment remaining after fermentation is *cellulose*, into which sugar has been converted.

That which is gained as *cellulose* by the ferment cells is lost to the sugar (out of which it is formed) as

regards the fermentation. But the quantity is too insignificant to be considered of any practical importance.

That the walls of the cells, which consist of cellulose, have no effect on the fermentation, will be clearly proved by the following experiments, made by me nine years ago.\*

If ferment be mixed with water, and the liquid filtered after standing some hours, and mixed with sugar, fermentation will begin.

If such ferment as remain on the filter be again mixed with water, allowed to stand, filtered, and sugar added, fermentation will be produced again in this liquid. By the repetition of this experiment the capability of the filtered liquid to engender fermentation is continually diminished, and a watery extract of ferment can never decompose as much sugar as the ferment itself, from which such extract is prepared.

The ferment, after being thus washed, still retains a large portion of a protein compound in the cells. For if they are put in this state into a solution of sugar at too low a temperature to develop fermentation, and then filtered, the liquid so obtained will possess a much greater power of fermentation than the simple watery extract.

By a repetition of this experiment, cells may be deprived of the greater part of their protein compound.

At last a body remains, insoluble in water, and nearly devoid of nitrogen, which, when put into sugar

\* Scheik. Onderz, deel. ii. p. 429.

and water, produces scarcely any fermentation. Solution of sugar is much more efficacious than water alone in extracting the protein compound enclosed in the cells.

The strong endosmotic properties of sugar are well known.

We may add to this that sugar appears to excite the ferment to the absorption of oxygen, although during the absorption its decomposition is carried on. Further, that lactic, or some other organic acid (tartaric acid in wine), assists in dissolving the albuminous matter, in extracting it from the cells and introducing it into the liquid, by means of which its own oxidation, and with it the decomposition of the sugar, is promoted.

Lastly, Stahl has expressed himself with regard to the principle of fermentation very clearly, and in a form which was announced as new, some years since, and ascribed to Liebig; he calls it "the molecule in motion." Stahl says, in reference to this, "A body in the act of decomposition may very easily communicate this condition to another body in which it has not begun. Indeed, such a body, in which internal movement has already commenced, may easily bring another body, which is still in a state of repose, but disposed to motion, into the same condition of internal motion."\*

The honour of having laid down the fundamental principle of fermentation, and all that which, taken

\* *Zymotechnia Fundamentalis*. Frankf. 1734, p. 304.

in connexion with it, renders the whole subject so much more intelligible, belongs to Stahl, who first clearly and distinctly enunciated it.

But the movement of the molecule is peculiar, and the word movement is as ill fitted to convey a correct idea of what is intended, as the word movement is to express the outstretching of the hand of friendship, or the drawing the sword of destruction, though both are actually movements of the hand. Schmidt mentions that gluten, meat, or ferment, in an advanced stage of decomposition, if put into a solution of 1 part sugar in 4 parts of water, loses in a few hours all signs of putrefaction, and yields a liquid of an agreeable odour, and which, if distilled, furnishes alcohol.

This fact is of importance on two accounts, it teaches us that sugar reverses the action of putrefaction, annuls it, and sets up fermentation. Putrefaction would progress were it not for the sugar, which decides the movement of the molecule to fermentation. Just so in the case of fresh ferment, sugar is active, not passive. We learn further that yeast cells are formed from putrid gluten or putrid meat. That these substances are coupled compounds of sugar is beyond doubt. Here also sugar is converted into ferment cellulose.

We will first apply these general results to the fermentation of grapes, before we proceed to develop, in detail, the history of spirits of wine.

Vegetable albumen and mucilage are found in the

pulp of grapes, and should these be brought into a state of transformation, by contact with air, they not only ferment, but excite the formation of alcohol and carbonic acid from the sugar. But gum and sugar are also found in grape juice, and fermentation may therefore be induced in it. And if ferment be once formed it may be decomposed at a later period, and fermentation kept up. No ferment can be detected in grape juice, but it is found after fermentation. The formation dates from the commencement of fermentation, and continues several days; its decomposition extends over a period of months, for this latter process does not consist merely in the emptying of the yeast cells, nor is this, indeed, its principal characteristic. The decomposition of yeast depends principally upon the chemical change of the albuminous matter which was formerly contained in the yeast cells.

The active fermentation of grape juice, which attains its highest point in 10, 12, or 14 days, is the period during which the decomposition of vegetable albumen and mucus, the formation of ferment and the emptying of ferment cells takes place; that is, the exudation of the albuminous contents through the walls of the cells. The after-fermentation is the period during which these albuminous contents decompose. During the after-fermentation a great deal of sediment is formed from the wine, but this contains no ferment. What this sediment is, we shall mention

by-and-by, only it must not be confounded with ferment.

Atmospheric air first comes in contact with the grapes at the time of pressing, whilst in the fruit the juice was protected by a covering saturated with wax. We recognise in the contact with air the primary cause of fermentation, that is, of the transformation of vegetable mucus, and rightly; for the mucus and sugar were present in the juice of the same grape. If, then, the conclusions drawn by Döpping and Struve from their experiments (p. 55) are decisive, why did not fermentation take place within the grape itself?

It is true that both Fabroni and Raspail have intimated that albumen and sugar occupy different positions in the grape. But this only holds good of the albumen found in a solid state in the walls of the grape cells (p. 35). In the juice, sugar and vegetable gluten are mixed (p. 37).

The admixture of the grape juice, which is well provided with free tartaric acid, with the crushed cell-walls of the pulp, promotes the solution of the solid vegetable albumen of the cell-walls.

The grape juice, from which every kind of wine is prepared, is by no means clear as water, but a turbid liquid, consisting of the pulp of the grapes, the contents of the pulp cells, and the torn cell-walls.

Fermentation and its development are undoubtedly promoted by the admixture of the contents of the cells



with the torn walls of the pulp. Sugar, gum, and vegetable mucus, are found in the juice, albumen in the torn walls. These four together are the material out of which ferment cells are constructed, a portion of one of the last two serving to engender fermentation, whilst the ferment is in process of formation.

If we call to mind the very considerable quantity of albumen found in a solid state in the walls of those cells in which the juice is enclosed (p. 35), and that free tartaric acid is capable of dissolving solid albuminous bodies (p. 36); and remember, further, that free tartaric acid exists in every kind of grape juice (the re-action of which is therefore always acid, even though the excess of sugar gives it a sweet taste), we shall be able to form an idea of the advantage derived from mixing a liquid containing acid with the torn walls of the cells of the grape pulp, rich as they are in albuminous matter. Döpping and Struve thought they saw ferment originate in carbonic acid or hydrogen gas, if we only so far throw doubt on the results obtained by them, as to think they did not, perhaps, completely exclude the air,—and, according to Gay-Lussac, very little air is necessary to cause fermentation,—then we willingly accept these statements by which they assert that no good formation of ferment takes place without larger admission of air. A little air may occasion fermentation, but to the formation of good ferment a well-regulated admission of air is necessary. In the same way, though but little oxygen is

necessary to excite fermentation, a larger quantity is needed in order to ensure the formation of ferment. Schmidt observed that a solution of grape sugar, under the influence of a solution of emulsin, which had been filtered, began to ferment at the end of four hours, and at the end of eight hours the fermentation was very perceptible, whilst cells could not be observed till the expiration of 36 to 48 hours.\* But there are here two points which must be kept distinct from one another. Fermentation may exist prior to the presence of ferment; and it may be set up in consequence of the addition of ferment. Fermentation may therefore exist before the formation and during the decomposition of ferment.

Schmidt's experiments, and those which are recorded (p. 68), teach us the first fact; the latter we learn from seeing fermentation brought about in a solution of sugar, by the addition of ferment.

What, then, will take place in freshly pressed grape juice? We may assume, without hesitation, the two aforementioned points; fermentation begins in consequence of the change induced in vegetable gluten or albumen, by means of a little *oxygen*, and hardly has it begun before the formation of ferment commences, and fermentation is maintained by means of its decomposition.

Wagner denies altogether the accuracy of the results obtained by Döpping, Strüve, and Schmidt,†

\* Ann. der Ch. und Pharm. Bd. 61, s. 168.

† Journ. für Prakt. Chemie, Bd. 45, s. 241.

and maintains that he has observed that fermentation and the formation of ferment cells begin simultaneously. He observed that acetic, lactic, phosphoric, and tartaric acid materially assist the formation of ferment, whilst the presence of sulphuric, muriatic, and nitric acid retards this process.\*

No more details are necessary concerning this matter, as these appear to me conclusive.

It cannot, indeed, be affirmed that this opinion respecting the action of ferment has always been admitted. Perhaps nothing in science has been so variously represented as the theory of fermentation; the most extravagant ideas have been repeatedly formed concerning it, and each was grounded upon observation and experiment. We will notice the following as shortly as possible. We may dismiss with one word the promulgators of the opinion that fermentation is an operation caused by a plant in process of formation (even supposing that plant to consist of a single cell, to which other cells may, at a later period, affix themselves independently), such as Schwann,† Quevenne,‡ Kützing,§ Turpin,|| Cagniard la Tour.¶ They have the merit of having described and drawn attention to the cellular nature of well-

\* See also Helmholtz. *Journ. f. Prakt. Chemie*, Bd. 31. s. 429. Brendecke (*Archiv. der Pharm.* Bd. 90, s. 10, and Bd. 93, s. 133.) Dubrunfaut, *Ann. de Ch. et de Phys.* t. xxi. p. 169.

+ Pogg, *Ann.* Bd. 41, s. 284.

† *Journ. de Pharm. An.* 1841.

§ Erdmann's *Journ.* 1838.

|| *L'Institut.* 1835, 1836, 1841.

¶ *Journ. de Pharm.* t. xii. p. 244.

formed ferment. But they went too far, in asserting that fermentation was a necessary condition of the origin or formation of such cells.

Blondeau, in 1847, was still of opinion that fermentation preceded the formation of ferment plants, and that it was developed step by step with them.

Two kinds of these plants are found in the yeast of beer, *Torvula cerevisiæ* and *Penicillium Glaucum*. The first are the genuine globules of ferment, the latter is a white film, such as may be seen in other substances verging on putrefaction; it is of a tube shape, with ramifications, and Blondeau can only have seen it in ferment which had been spoiled.

That fermentation is very much determined by the quality of these cells was what Lüdersdorff attempted to show, by proving that the cells of ferment, after being rubbed in water for six hours, are incapable of producing fermentation.\* But Schmidt has rightly observed,† that so much friction would considerably facilitate the oxidation of the fermenting matter. Lüdersdorff's experiment and its negative result only serve to establish the assertion laid down (p. 64), "that the cause of fermentation is to be found in the oxidation or decomposition of the contents of the ferment cells." Schmidt found in a single gramme (15·4 grs.) of ferment (after it had been in contact with water for six hours), by adding sulphate of magnesia and phosphate of soda to the liquid, and collect-

\* Pogg's Ann. Bd. 67, s. 409.

+ Liebig's Ann. Bd. 61, s. 171.

ing the deposit, 0·013 (0·2 grs.), and in a gramme of ferment, which had been rubbed in water for six hours, 0·056 (0·86 grs.) phosphate of ammonia and magnesia. There are, therefore, decomposed fermenting matters in the ferment; but there is also another substance contained in it, which is still decomposing, and this only requires to come in contact with the air in order to be resolved into ammonia.

Schubert\* instituted a variety of investigations upon the subject of fermentation, which must serve as critical reviews of those earlier ones undertaken by Lüdersdorff† and others.

Lüdersdorff thought he had observed that ferment ceased to operate if its particles were subjected to friction, and believed with Cagniard la Tour, and others, that the action of the ferment depended as a general rule on the cellular structure of its parts.

Schubert, on the contrary, attempted to prove that even vegetable particles are unnecessary to fermentation. He ascribes its operation solely to the peculiar capacity possessed by ferment of absorbing gas, and he thought that when he substituted other bodies possessing the same capability in an equal degree, he really perceived a fermentation of sugar. He was led to make these experiments by the following statements.

According to Rousseau, whose opinion is confirmed

\* Pogg's Ann. Bd. 69, s. 157 and 542; Bd. 77, s. 197.

† Ibid. Bd. 67, s. 408.

by Colin and Thénard, ferment, in order effectually to promote fermentation, must be acidified by means of a vegetable acid.

Brendecke had observed that the addition at one and the same time of acid, tartrate, or citrate of ammonia, and of a porous body, such as charcoal, straw, asbestos or goldleaf (?) to solution of grape sugar causes active fermentation, and according to him the salts remain unchanged.

Schubert having multiplied these experiments, and carried them out in detail, found that not only grape, but cane sugar was decomposed in the same way. The same effect may be produced by platinum black, pumice stone, fresh precipitated alumina, paper, silver-leaf, flower of brimstone, asbestos, and starch. The operation is more tardy than in the case of ferment, but it does not fail.

The co-operation of a vegetable acid Schubert found unnecessary, as the other substances named above can act without it. Spongy platinum, pumice-stone, burnt clay, oxide of iron, and pectin, caused fermentation in the space of a few days. Nevertheless, acid vegetable salts do very materially assist fermentation, even when they are present in the shape of powder, and cream of tartar is very useful, whilst other salts, such as metallic and common salt, are prejudicial.

According to Schubert, the formation of ferment simultaneously with the commencement of fermentation, is by no means necessary to fermentation. Not-

withstanding this, when he saw fermentation begin in quite another way, he thought "that the nitrogenous constituents of the ferment were chemically decomposed, and the decomposition transferred to the sugar by the application of the ferment;" and his view of fermentation, taken as a whole, scarcely differs from that here given, inasmuch as both seek the cause of fermentation, not in the formation, but in the solution of ferment.

I may just observe, that I do not lay much weight on many of Schubert's early results. It may be as well not to admit that fermentation can be brought about by means of spongy platinum, or oxide of iron.

H. Rose explains at length why fermentation is promoted by certain organic acids.\* He draws attention to the fact, that fermentation is a much slower process in cane than in grape sugar, and that a much larger quantity of ferment is required to produce fermentation in the former than in the latter. If a little tartar is added it quickly sets the cane sugar in fermentation.

The reason of this is very clear. Rose made use of beer ferment treated with water. The albuminous substance enclosed in the cellulose is with difficulty soluble in water, and yet it must escape before fermentation can begin. Tartaric acid dissolves it easily, diluted acetic acid with less ease, and sulphuric acid not at all. Rose also found that sulphuric acid and

\* Pogg, Ann. 1841, vol. lii. p. 297.

acetic acid did not produce the same effect as tartaric acid.

These results agree entirely with those obtained from the grape fermentation. It was long known that fermentation is promoted by a copious supply of tartaric acid in grape juice. Fermentation is more rapid in the juice of not very ripe grapes, which contain a considerable quantity of free malic acid (Schwarz) than in that of perfectly ripe grapes; and wines containing a great deal of sugar, and therefore, as a rule, less free acid, ferment more slowly than those in which the proportion of sugar is smaller.

After these general observations upon ferment and fermentation, we may turn our attention directly to wine ferment, and the manner in which it is formed. And first, we have the investigations of Bouchardat, which though by no means complete, teach us, what from want of knowledge in this matter I formerly left undetermined, that wine, as well as beer, ferment consists of cells, of which only the contents are active;—an observation which coincides with Quevenne's.\*

The diameter of the globules of wine ferment was found by Quevenne not to exceed from  $\frac{1}{200}$  to  $\frac{1}{150}$  millimeter (0.039-inch). He observed that their contents, when acted upon by hydrochloric acid, assume a beautiful violet colour (this being a characteristic of albuminous bodies); and he also remarked that the

\* Erdmann's Journ. Bd. 14, s. 346, 1838.



globules (of ferment) retained their form even under the influence of potash. Quevenne was not, however, acquainted with the properties of ferment.

Ferment of wine is designated by Bouchardat\* "ferment noir." He obtained from white wine, ferment consisting of round particles, characterised by a black spot.

The globules are mostly homogenous, perfectly round, and have a diameter of from  $\frac{1}{228}$  to  $\frac{1}{250}$  millimeter. Put into sugar and water at a temperature of from  $10^{\circ}$  ( $50^{\circ}$  F.) to  $12^{\circ}$  ( $53^{\circ}$  6' F.), the ferment put an end to fermentation, which had been carried on during a period of six months; and more than 17 per cent. alcohol was found in the fermented liquid. According to Bouchardat tannic acid exercises a considerable influence upon fermentation. The white of 4 eggs and 1 kilogramme (2.2 pounds) of sugar were dissolved in 7 pints (4 litres) of water, which contained  $\frac{1}{1000}$  of muriatic acid. The mixture was divided into two equal portions, and to one-half was added, 10 grammes (154 grs.) of tannic acid, dissolved in 100 grammes (1543 grs.) of water. A copious precipitate was formed, and the slow fermentation, begun by means of the black ferment, was completed at the end of 40 hours, in a temperature of  $25^{\circ}$  C.,  $77^{\circ}$  F. In the other half of the liquid not a trace of alcohol could be detected. But how can tannic acid, which

\* Compt. Rend. tom. xviii. p. 1120.

possesses the property of precipitating albuminous substances, promote fermentation?

Among the constituents of wine ferment, Bouchardat reckons an albuminous substance, a solid fat, a liquid phosphoric fat, lactic acid, lactate of lime and lactate of soda, acid phosphate of lime and of soda. All which bodies have either already been found or might be discovered in beer ferment.

I now address myself to Walz's Analyses, which, being perfectly valueless, I should pass over in silence, were it not that their apparent accuracy is calculated to mislead and give rise to grave mistakes.

Walz found that wine and beer ferment correspond exactly.\* He detected in them fat of a greenish colour, brown resin, albuminous matter of easy solubility in acetic acid, besides gypsum, tartrate of lime and magnesia, oxide of iron and some alumina. Wine ferment washed with water, acetic acid and potash, left a residue of cellulose, after the cells were emptied. And this, according to Walz, exactly agrees with the residue of beer ferment. He gives their chemical composition in the following manner:—

Cellulose.		
In wine ferment.	In beer ferment.	In dry ferment.
Walz.	Schlossberger.	Mulder.
C. 45·5	45·5	45·0
H. 6·6	6·9	6·1
O. 48·1	47·6	48·9

\* Journal für. Pract. Pharm. vol. xiii. p. 77. In the following analyses, C=6, N=14.

The following numbers were obtained, I.—from the extract of wine ferment in acetic acid, precipitated with potash; and II.—from the potash extract, precipitated with acetic acid:—

	I.	II.	With potash. Schlossberger.	With acetic acid. Mulder.
C.	55·5	55·5	55·5	54·4
H.	7·5	7·5	7·5	7·0
N.	14·0	14·0	14·0	16·0
O.	23·0	23·0	23·0	22·6

Wine ferment burnt as such, yielded—

Walz.	Mulder.			Walz. Quite another Wine ferment.	
	Different kinds of ferment.				
	I.	II.	III.		
C.	49·4	51·9	51·3	50·9	49·6
H.	6·6	7·2	7·0	7·0	6·6
N.	10·5	11·1	9·5	8·5	10·4
O.	33·5	29·8	32·2	33·6	33·4

I have used round numbers throughout, not only because the whole analysis appears to me suspicious, but also (I venture to assert it, having convinced myself I am right) because it was made with the pen and not with the ferment.

In the first place, in the carbon and hydrogen of the cellulose ferment, he exactly splits the difference between Schlossberger's numbers and mine. He divides his confidence between Schlossberger and me.

The next point is of more importance. He finds the two substances treated with potash, or acetic acid, exactly correspond to one another; although every one

is aware that when treated with potash, the nitrogenous contents are diminished, which is also shown in the different results obtained by Schlossberger and by me. But it was convenient to him in this instance to copy only Schlossberger's numbers.

But what follows is still worse; ferment, burnt as such, should have a composition of its own. Ferment consists of cells and their contents, each formed of a totally different substance. Walz professes to have found, in two different kinds of ferment, the same contents, and the same amount of hydrogen, exactly corresponding in quantity with that in ferment cellulose, although a considerable quantity of albuminous matter must in every case be found in ferment as a whole, and this albumen has 7 per cent. hydrogen. Should 25 different kinds of ferment be analysed, some difference would be detected in each, just as the contents of sacks filled with the same article, for example, money, would not necessarily be alike. But I will not detain the reader longer with these numbers.

Braconnot's\* analyses of wine ferment, made some few years since, well deserve to be more particularly mentioned. He treated a sediment obtained from wine with carbonate of potash or soda, in order to saturate the acids, and found that a large portion of the actual fermenting matter was thereby dissolved.

\* Annales de Chimie, t. xlvi. p. 69.

He filtered it, and precipitated it with acetic acid, by which means he obtained one of the constituents of ferment in the form of an albuminous substance, which had not lost the power of coagulation. The precipitate obtained by acetic acid from the alkaline solution, and coagulated by boiling in water, rendered the water limpid. He found that the substance, before it was heated in water, was soluble in lime water, but after it was so treated it was no longer so. Tartaric acid dissolved this substance easily, and when saturated with alkali the solution was sticky. The uncoagulated ferment caused speedy and active fermentation in a solution of sugar.

The constituents of the ashes of ferment have been analysed by Mitscherlich;\* but as the special object of investigation was beer ferment, only the principal points are of use to us. He found 7.65 per cent. ashes in the "upper ferment," 7.51—7.61 in the "under ferment," obtained by burning upon silver, supported on platinum, in a glass tube under a stream of oxygen; and at the same time collecting the volatile products, he gives

	Upper ferment.	Under ferment.
Phosphoric acid.....	41.8 .....	39.5
Potash .....	39.5 .....	28.3
Phosphate of Magnesia, 2 Mg O. Ph O <sup>5</sup>	16.8 .....	22.6
Phosphate of Lime, 2 Ca O. Ph O <sup>5</sup> ..	2.3 .....	9.7

The principal components found in the ashes of fer-

\* Erdmann's Journ. 1845, th. iii. s. 231.

ment are therefore acid phosphate of potash, neutral phosphate of potash, phosphate of magnesia, and phosphate of lime.

From what has been said about the composition of wine ferment, it is sufficiently evident that it does not essentially differ from beer ferment, for both consist of membranous cells which are formed out of gum, or vegetable mucilage. Both possess albuminous contents, which exude through the walls of the cells, and when brought into contact with sugar, cause it to ferment; these contents are soluble in water, more so in vegetable acids, and peculiarly so in tartaric acid. So much of the albuminous substance as is soluble is decomposed during fermentation, and more or less of its products must be contained in the liquid.

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ON THE DIFFERENCE BETWEEN THE CONSTITUENTS OF  
GRAPE JUICE AND THOSE OF WINE, CONSIDERED IN  
CONNEXION WITH FERMENTATION.

The formation of ferment diminishes the gum or vegetable mucus in the grape juice, and renders it insoluble, in which state it composes the walls of the ferment cells, and the juice becomes turbid. In this manner vegetable gluten and vegetable albumen (substances contained in the grape pulps) are withdrawn from the juice, and enclosed in the cells. But during the decomposition of ferment,

the cells are emptied, and sink as sediment to the bottom, their albuminous contents undergo decomposition, and some of the constituents are retained in the wine, in a soluble form. During fermentation the liquid becomes turbid, and this result we ascribe to the formation of ferment. But as soon as alcohol is produced from the sugar contained in it, the power of the liquid to hold different substances in solution undergoes a great change.

There is a diminution first in the mucilaginous and saccharine contents of the juice, then those substances decrease which are insoluble in common water, but which can be held in suspension when in a fine state of division; for example, phosphate, sulphate, and lactate of lime. If, therefore, the gum serves for the formation of ferment, and the cellulose and sugar be resolved into alcohol and carbonic acid, then the liquid, which was rendered turbid at first by the formation of ferment, will continue so during fermentation, because the phosphate, sulphate, and tartrate of lime are being continually precipitated. The result of this process is an alcoholic instead of a watery liquid. Cream of tartar is much less soluble in weak spirit than in water, and this is a third cause of the turbidity of the juice which is gradually becoming resolved into wine. The continual increase of the quantity of alcohol in the liquid causes the precipitation of sulphate of potash and tartrate of magnesia, or tartrate of potash and magnesia.

The separation of these substances increases proportionately to the increase of alcohol, and continues till fermentation is at an end. These substances at first make the wine turbid, but speedily deposit themselves at the bottom as a crust, and form raw tartar.

Young wine contains, therefore, less of the salts which have been mentioned than the grape juice from which it is produced, and the poorer the wine is in gum and sugar and the richer it has become in alcohol, the smaller will be the proportion of these salts—namely, phosphate, sulphate, and tartrate of lime, double racemate of potash, sulphate of potash, and tartrate of magnesia. At the same time, the albumen and the gum (the latter in the form of cellulose), are separated, and appear partly as ferment; and in place of the albumen which, after being converted into ferment, is afterwards decomposed, the products of that decomposition enter into wine in the shape of extractive matters, with the nature and quality of which we are at present, however, but imperfectly acquainted.

Braconnot is the only person who has analysed the sediment which first forms in wine. It is a mixture, in which both the above-mentioned salts and the ferment, which has been separated, occur. He found 21 per cent. albuminous matter, more than 61 per cent. cream of tartar, besides 5 per cent. tartrate of lime, 6 per cent. phosphate of lime, 2 per cent. sulphate of lime, the rest alumina; and, moreover, a



white, greenish, wax-like fat was found in this liquid.

In conclusion, I cannot suppress the observation, that ammonia being developed during the formation of ferment, and magnesia and phosphoric acid being found in the grape juice, phosphate of ammonia and magnesia must be precipitated, and the wine, therefore, will contain much less phosphoric acid and magnesia than the grape juice.

By the time the first fermentation, which lasts from 10 to 14 days, is complete, all ferment has disappeared from the surface and sunk to the bottom with the above-named salts. The wine is now transferred to other casks, in which it undergoes slow fermentation.

The wine, when drawn off, is far from clear, as the ferment cells floating in it render it turbid. It is not, however, these cells which keep up after fermentation, but their contents which, having exuded through the cells, are found in young wine in a soluble form, and produce fermentation.

It follows necessarily that the deposit formed in the wine during after-fermentation, is quite unlike that which is produced during the first few days ; much less albuminous matter is mixed with the salts, and it consists of what is known as raw tartar. Its principal constituents are, indeed, salts which have been separated in consequence of the increase of alcohol in the liquid ; salts therefore which are insoluble in alcohol.

In red wine a portion of colouring matter and of tannic acid is withdrawn by these salts, which is thus rendered less astringent and of a lighter colour.

The tannic acid is precipitated with other substances which were held in solution, and in order to prevent them from being brought within the range of decomposition (which happens when the admission of air changes the tannic acid into apothema, and sets free the albumen, whereby a new spring of chemical action, often injurious to the wine, is set free) the wine during after-fermentation is several times transferred into other casks, and so freed from sediment. The transfer into fresh casks must be repeated so long as deposit of raw tartar forms; the wine cannot be bottled until this ceases.

In these respects the wine differs from the grape juice out of which it is prepared.

When the skins are allowed to ferment, a diminution of some and an admission of other constituents takes place. In the first place, the water of the wine may dissolve some substances from the crushed grape skins, for example, tannic acid. If the action of the water be assisted by alcohol, the solution will be stronger, and colouring matter extracted from the skins will also be dissolved with the tannic acid, and that in proportion to the quantity of alcohol formed out of the sugar.

In the manufacture of the best Burgundy and coloured Champagne the skins remain in the liquid

from two to three days, in that of Medoc 6 days, 8 days in those prepared in the south of France, which are especially meant for the table (*vin ordinaire*), 14 days is the longest time, and in this case the wine has a very dark colour. The greatest care must be taken to prevent the wine from becoming acid, for during fermentation by the escape of carbonic acid, a superficial covering (*chapeau*) upon the wine speedily forms, by which means the alcohol is exposed to the influence of the air under circumstances resembling those which facilitate the rapid formation of vinegar. To prevent the formation of this superficial covering (*chapeau*), the skins must be constantly stirred.

## CHAPTER III.

### CLEARING OF WINE.

THE clearing of wine, as well as the frequent transfer of young wine into other casks, is undertaken with the view of removing all the sediment in which albuminous matters may still occur. As far as the decomposition of the wine is concerned, it is immaterial whether the sediment has deposited itself, or still floats in the wine; whatever can contribute to promote after-fermentation must be removed, as long as there is sugar enough to cause new fermentation in spite of the quantity of alcohol already formed; for should any such fermenting matters remain in the wine, they would tend to the production of another chemical change. The wine which is rendered turbid by the ingredients of ferment is not durable. New wines must therefore be treated until they become as clear as if they had been filtered.

There is another reason for undertaking the clarifying of wine, which concerns the alteration of its colour, and is practised upon red wines. Light-coloured wines are preferred, and albumen and isinglass are added, which, as well from their insolubility in alcohol, as from their combining with tannic acid,

form a spongy flocculent sediment, by means of which a larger or smaller quantity of colouring matter, in proportion to the quantity of albumen or isinglass which has been applied, is withdrawn from the wine.

Clearing may also be undertaken in order to diminish the tannic acid contained in the wine; and this again is effected by means of albumen and isinglass.

For when both these substances are added to port wine, tannic acid and colouring matter are continually abstracted from it, so that by adding them in large quantities, tannic acid may be entirely withdrawn, and a very light-coloured wine be obtained.

The colour of wine, in which but little tannic acid is contained, can only be abstracted by adding a solution of tannic acid, previous to the addition of albumen or isinglass, in which case, so large a quantity of colouring matter is precipitated, as to render the wine very light coloured. Albumen and isinglass alone could not have effected such a change. The cause of this phenomenon will be made quite clear when we come to treat of the colour of wine; for colouring matter is soluble in alcohol and tartaric acid, and more or less so in water and tartaric acid. The chemical affinity which exists between the particles of colouring matter, and such albumen or gluten as has been precipitated by means of alcohol and tannic acid, is more or less overcome by the power, which a mixture of water, alcohol, and tartaric acid possesses of retaining colouring matter in solution.

But wine may, however, be rendered colourless by saturating its free acids with a base.

By overlooking this fact, namely, that the colouring matter of wine is soluble in alcohol and water with tartaric acid, many, and amongst them Batillac,\* have been led to entertain very erroneous views respecting the nature of the actual colouring matter of wine, and the theory of that discolouration of wine which occurs during clearing.

Isinglass produces much greater discolouration in wines which are poor in alcohol and tartaric acid, than in others. Where, however, the object in view in clarifying, is not so much the removal of tannic acid and colouring matter, as the separation of such of these particles as, being in a state of minute division, do not readily sink, other means are resorted to. In Spain, powdered marble is mixed with white wines, and gypsum or sand is used in other countries. In warm climates the use of albumen and isinglass is generally avoided, inasmuch as a portion of these substances might easily remain in the wine and spoil it. Powdered gum arabic is then used as a clarifier; gum is imperfectly dissolved in weak spirit, and such particles as still float in the wine are precipitated with it. Of the means mentioned, only albumen and isinglass act chemically upon the wine, the others are purely mechanical. A little dissolved gum may easily remain in the wine, the viscosity of

\* *Traité sur les Vins de la France*, p. 34.

which will be thereby increased. Albumen, mixed with tartaric acid, dissolved in water, cannot be precipitated, either by boiling or by alcohol, for the tartaric acid holds the albumen in solution. From this we learn that albumen, when used in the clearing of wine, is not rendered insoluble by the alcohol in the wine, but by the formation of tannate of albumen.

The precipitate of tannate of albumen thus obtained, is, however, soluble in water, with excess of tartaric acid. How far the discolouration of wine may be carried by means of albumen, depends on the quantity of tartaric acid, tannic acid, and alcohol present in the wine. Vergnette Lamotte\* prefers isinglass to albumen, and recommends it as better adapted to the purpose. Isinglass cannot, however, be completely precipitated in weak spirit. It is, therefore, also chiefly useful because it forms a precipitate with tannic acid.

If but little tannic acid be contained in the wine, the precipitate obtained by means of isinglass will be inconsiderable, and but a small quantity of colouring matter will be withdrawn from the wine. So that the use of isinglass will only render the colour of wines containing much tannic acid lighter. To render it useful as an application to other wines we must first, as we have seen, add a little extract of nut-galls to the wine, which at once imparts the power to isinglass of

\* Dingler's Polyt. Journ. Bd. 111, s. 147.

precipitating tannate of gelatine and colouring matter. In some countries extract of grape stones, which, as we have seen (p. 44), contain a large proportion of tannic acid, may be used instead of nut-galls.

Clearing, as a general rule, makes wine more durable; but when isinglass or albumen have been employed, this is not always the case. Burgundy wines, which are readily decomposed, are often rendered more easily decomposable in consequence of clearing. For Burgundy wine contains but little tannic acid, and the process of clearing, by freeing it still more from this, removes at the same time the ingredient which would have rendered inert the albuminous substance of the wine.

Too large an admixture of solution of gelatine, or albumen, brings the germ of decay into the wine which is cleared; since they are both organic bodies, easily putrescible, and capable of exciting decomposition in other substances.

If too much gelatine or albumen has been added, Vergnette Lamotte recommends the use of a little tannic acid. Bussy,\* speaking of the clearing of Burgundy wine, urges the application of extract of nut-galls to the wine, before gelatine is used. Before this method was known, it was impossible to render Burgundy quite clear without exposing it too much to the chance of spoiling, since all the tannic

\* *Moniteur Industriel*, 1848, No. 1300.



acid was withdrawn, and very often replaced by gelatine, or albumen. An addition of tannic acid is also recommended in the case of those white wines which occasionally become "lang," what the French call "graisse." Tannic acid tends to produce stability by combining with the small quantity of albuminous matter which is found in the wine, and which, though not thereby made insoluble (as is the case in tanning leather), since the tartaric acid keeps it in solution, is yet rendered less susceptible of decomposition.

Only the best isinglass, such as is thoroughly tasteless, should be made use of in clearing wine.

Blood is now and then used instead of albumen; and in a low temperature dried blood, which is sold as powder, is occasionally employed. But none of these means are applicable to good wines.

Milk and cream may also be used as clarifiers, since the caseine contained in milk combines with the tannic acid of the wine, and acts in the same manner as albumen or isinglass.

Some, whilst clarifying with albumen or isinglass, add a little common salt to the wine, a proceeding, however, which is said by Batillat\* to be useless.

If lime be mixed with wine in order to abstract tartaric or acetic acid, a precipitate is formed in the first instance, which carries down a larger or smaller portion of the colouring matter of the wine (if red).

\* Mon. Industr. p. 101.

The lime, therefore, in the first instance, produces discoloration, but it also combines with the tannic acid, forming tannate of lime; a salt which, though insoluble in excess of lime, remains in solution, if sufficient lime be added to saturate the liquid. Lime, therefore, is always capable of imparting to wine the same property which is given by albumen or isinglass—the wine is rendered less astringent by the precipitation of tannic acid, and becomes at once less acid to the taste.

From these two causes the use of lime in the preparation of wine has become much more general, since it gives a sweeter and less astringent taste to the wine, and an appearance of age.

Lime, like other alkalis, if employed in excess, turns wine brown.

## CHAPTER IV.

### SULPHURISING.

SULPHUROUS<sup>s</sup> acid hinders fermentation by combining with the albuminous substances present in wine, and thereby rendering them inert, and by attracting to itself the oxygen which is necessary to decomposition. The absorption of oxygen changes sulphurous into sulphuric acid, which also combines with albumen, and forms a compound which is incapable of fermentation.

Sulphurising is effected by burning sulphur in bottles or casks, and instantly pouring in the wine, which absorbs the sulphurous acid thus formed.

If wine has been too strongly sulphurised, the unpleasant smell and taste of the sulphurous acid may be clearly perceived in it.

As it is often necessary to ascertain the amount of sulphuric acid in wine, in order to distinguish between such as are genuine and adulterated, the process of sulphurising deserves particular notice. By it the sulphuric acid in the wine is increased, and its quantity is, therefore, no standard when suspicious wines, which have been sulphurised, are examined.

If the sulphur should contain arsenic, the wine is thereby rendered arsenical.

It is stated in many books, but I am of opinion that it originated in a misprint, which, as is often the case, has been sedulously transcribed, that in old times the Dutch exposed the casks, in which they exported wine to the East Indies, to the fumes of sulphur, arsenic, and antimony. I doubt this exceedingly, for our ancestors were no fools, especially in matters concerning their profit, and this was not likely to be promoted by the addition of arsenic to wine.

In the process of sulphurising, cloves, cinnamon, lavender, thyme, and other aromatic substances, are sometimes put with the strips of linen which are dipped in melted sulphur and allowed to burn. They cannot, however, destroy the smell of the sulphurous acid, although they may well impart a peculiar odour to the wines, in the sulphurising of which they are employed.

Sulphurising is particularly applied to sweet white wines, which, possessing an excess of sugar and albuminous matter, and but a small amount of tannic acid, are easily decomposed. The same process applied to red wine makes them rather lighter coloured.

One great advantage gained from sulphurising the casks in which wine is to be stored, is that it prevents the formation of mould, which afterwards imparts a musty taste to the wine.

Wine intended for exportation to warm countries is in general more strongly sulphurised.

Sometimes a portion of the wine is strongly sulphurised, and added to a certain quantity of the wine which is to be sulphurised. Sometimes sulphurous acid, dissolved in water, is employed; and sulphite or bisulphite of potash are occasionally used for the same purpose.

Another method is employed in some districts of France, which answers the same purpose as sulphurising—that is, hinders the fermentation of sweet wine, and preserves the greatest amount of sugar. It consists in putting  $\frac{1}{1000}$  pulverized mustard-seed into the wine, but I do not know how this acts.

## CHAPTER V.

### CELLARING OF WINE.

ROGIER applies the proverb, "Everything which lives is born dying," to wine, by saying, "That every wine bears within itself the germ of corruption!" As a rule, we may say, "Everything which is organic perishes," the cause of its destruction is to be looked for in itself.

A complex mixture of organic substances may be enclosed in hermetically sealed vessels, and withdrawn as much as possible from external influences; but even if alcohol, a substance peculiarly opposed to decay, be contained in it, time will still produce an effect,—which means that chemical rest is impossible in a complex mixture. Though the action cannot be observed at any moment, yet the effect of what has been carried on during hours, days, and months, is perceptible at the end of years. You do not see the wood from which ships are built, and buildings erected, dissolved into gas, but chemical change is ever going on, and at the end of years or centuries it has become volatilized, and no longer exists as wood. So all wine must eventually be spoilt; but some kinds acquire, as a first consequence

of the operation of that cause which afterwards destroys them, and which is neither more nor less than the chemical alteration in their constituents, properties which render them more agreeable both to smell and taste.

As it is very seldom possible to analyse wine after it has attained a great age, the few analyses we possess of this nature are of extreme value. Some Malaga wine which was buried during the conflagration of London, A.D. 1666, and only dug up 40 years since, though nearly 200 years old, was found perfectly good and well flavoured.\*

We have traced the chemical history of wine from its first beginning to the time when, having been clarified in casks, and poured into wooden vessels and bottles, it is fit for use; and we must now endeavour to make ourselves acquainted with the operation of that slow process to which I have already alluded, and with the circumstances which may expose wine to its influence.

As a general rule, wines which have retained a considerable portion of albuminous matter, and possess but little tannic acid, cannot resist the influence of time. They become acid, or undergo some other change. This occurs in the case of Rhine wines, which contain but little alcohol; and all those wines which contain much sugar, or but little tannic acid, cannot be kept long.

\* Journ. of Science, vol. i. p. 136.

Wines which can be cellared are those which improve, or to speak more correctly, those wines are stored which do improve with age. In these, odoriferous substances are formed, the wine becomes less acid and better tasted; such as is coloured often deposits a considerable amount of sediment, and if the wine be stored in casks, there is constant increase of alcohol.

We must begin by considering the change which takes place in the wine.

The ancients knew that wine improved if kept in leathern bottles, and the same result is obtained by keeping it in wooden vessels: for both leather and wood are more easily penetrated by water than by alcohol; evaporation ensues from both, but more freely from water, and the wine consequently becomes richer in alcohol. Sömmering's experiments rendered this very intelligible; since, by putting weak spirit into a bladder, and hanging it in a warm place, he increased its strength. Later observations have caused Sömmering's result to be received with modification, so that the simple evaporation of water is no longer spoken of, since it has been ascertained that a certain quantity of alcohol, though proportionately less, evaporates with the water.

Even supposing equal quantities of alcohol and water to be evaporated, the wine would still be improved, as all the other constituents would remain undiminished. But Graham\* a short time since

\* Chem. Gaz. 1854, p. 420.



proved that if diluted alcohol were put into a bladder, the water would really evaporate, and the spirit be concentrated. Schubert,\* on the contrary, asserts that wood allows a readier passage to alcohol than to water, and maintains as proof of this, that spirit of wine loses strength when in a wooden cask. Even if it be so, it does not follow that wine, which contains less alcohol than water, should allow proportionately equal quantities of each to evaporate.†

Wine stored in wooden casks loses therefore in water, whether mixed with alcohol or not. But if evaporation affects the contents of the cask, the loss must be repaired, otherwise the action of the air would turn the wine sour, and convert the alcohol into acetic acid.

It is chiefly water which is evaporated, and its loss is made up by adding wine. All the constituents of wine, with the exception of water, are hereby increased, and the wine becomes not only stronger, but better flavoured. The vinous components being more concentrated, are better able to act chemically upon each other, and this alone would account for the improvement of the wine. Here we have a general statement of the causes upon which the difference between new wine and that which has been stored in casks mainly depends. But the change is carried

\* Pogg, Ann. Bd. 77, s. 409.

† Consult Wackenrader's Archiv. Bd. 34, s. 16; Bd. 35, s. 29. Liebig's Annal. Bd. 37, s. 128.

still further ; the concentration of the wine, or rather, the diminution of water, which is continually replaced by wine, causes a constant increase of tartaric acid in the wine. Wines which are poor in sugar may easily become too sour, and all wines cannot, therefore, undergo this process. The quantity of tartar in the wine is not increased, for, being insoluble in alcohol, the continual increase of alcohol precipitates it. That which is increased is tartaric acid, which is soluble in alcohol, and not insoluble cream of tartar. Madeira, and such like wines, are sent to warm countries to improve. I have had Madeira, which had been seven times (in cask) to the East Indies and back, and truly such nectar was unknown to the gods of the ancients. The drier the atmosphere is which surrounds the casks, the greater will be the evaporation. To avoid this, care must be taken to prevent draughts, and to keep the air of the wine stores or cellars moist.

The larger the casks, the smaller will be the surface in proportion to the contents. The observation has been made with respect to Sauterne wine, that whilst in casks containing 200 quarts, the evaporation =  $\frac{1}{12}$  th ; in casks holding 4716 quarts, the evaporation only amounted to  $\frac{1}{20}$  th.\* In order to replace regularly the wine which is lost from the cask by evaporation, it has been recommended to fill a bottle with wine, render it air-tight, place it with its neck down

\* Sichel in Dingler's Polyt. Journ. Bd. 89, s. 320.

in the opening of the cask, renewing the contents so as to keep pace with the evaporation. Well washed river sand is also used when there is not wine enough to fill all the casks. St. Vincent\* recommends that the bottles in which wine is put should not be corked, but closed with a bladder, because the water would evaporate as slowly through the bladder as through the casks, and equally beneficial results would be obtained. But I am not aware that any one else has ever tried the experiment.

Young wine, and older wine, when placed alike in wooden casks, comport themselves very differently. For when fermentation first goes off, a great deal more sediment is deposited than at a later period, and tannic acid, combined with an albuminous body, is always found in this sediment; and as this compound is capable, (by the change of tannic acid into apothema,) of causing such chemical action as shall be injurious, the wine is drawn off into other casks, in order to free it from sediment. And the reason that this change cannot be more frequently effected is, because in every transfer the wine becomes saturated with air, which causes it to turn sour.

The opinion that wine which has grown old in bottles has therefore become richer in alcohol, is thoroughly false. I do not deny that the alcoholic contents of many old wines is considerable, but I

\* Pelouze and Frémy, *Chemie. Gen. t. iii. p. 432.*

+ *Polyt. Centralbl. 1849, p. 790.*

deny that the wine being kept in bottles increases it. Evaporation is very much hindered by the cork, even when it is not covered with resin and sealing-wax. The sugar which exists, for example, in red wine, is in too insignificant a quantity to evolve alcohol by means of fermentation; and in old wine, the opening of the bottle causes no escape of carbonic acid. Therefore, the formation of alcohol in the bottles is impossible.

The simple explanation of our finding old wine rich in alcohol is, that only the stronger wines can be preserved, and the weaker ones cannot resist the effects of time.

The colour of wine is materially affected by another change which it undergoes when cellared (I am supposing it to be in bottles). The colour of liqueur-wines becomes darker, but such wines as are rich in tannic acid, port, for example, deposit a sediment, and become lighter. Red-wines, which contain no large amount of tannic acid, generally grow darker. The details, which must be mentioned in order to explain this change, will be better understood when we come to consider more particularly the colouring matter of wine. With regard to the fact just mentioned, that wines which are not rich in tannic acid acquire a darker colour, I will only observe that the diminution of free acid in the wine (be it tartaric or acetic) is always connected with this appearance, for the red hue is the effect of free acid, and the de-

crease of such acid allows the colouring matter to appear more purple.

I shall endeavour to explain more fully, in treating of the odoriferous constituents of wine, the manner in which the acids are altered in the course of time.

As a general rule, we may say that the development of aroma, and the sweetening of wine (supposing it to be cellared in bottles), are very closely connected. An increase in the saccharine contents is not to be thought of; how could it be effected? Diminution in the quantity of free acids must therefore take place, and this can only occur by the acids being either decomposed or combined with new non-acid substances. Both these alterations are the result of a slowly progressive chemical operation, which could scarcely be imitated by art. Warmth is the only means with which I am acquainted, which is really useful in producing the like results. In order to increase the appearance of age in wine speedily, it has been recommended to place bottles corked, but not quite filled with wine, for two hours in warm water, in a temperature of  $85^{\circ}$  C. ( $185$  F.), afterwards allow the wine to cool, and fill the bottles. Wine containing much spirit acquires thus the flavour and aroma of that which has been cellared ten or twelve years. I am willing enough to set much store upon this means of improving wine, and upon that which consists in keeping the bottles for a certain time in a warm place. It is still a question, though, whether such artifices impart

precisely those qualities to wine which it acquires by time. Those odoriferous constituents which are speedily developed by heat, may not be exactly the same as those which are engendered by the lapse of time. It seems reasonable, however, to make use of heat to diminish the acidity of the wine, just as it is rendered less acid by time.

As I mean to enter fully upon the diminution of the acid taste, and the increase of the quantity of odoriferous constituents, in treating of the odoriferous constituents, I will only allow myself to say a word in support of the opinion that cellaring in bottles helps to diminish the acid, or increase the sweetness of wine. It relates to the decomposition of tartaric acid, a decomposition which occurs quickly upon the ripening of the fruit, but proceeds gradually in the wine in the course of time. It is generally known that fruits do not ripen till they have attained their full size, and this is certainly the case with grapes. Before they are ripe they appear to contain malic and tartaric acid in excess, but whilst ripening the acids decrease, and the sugar increases in quantity.

In warm countries the quantity of tartaric acid contained in the grapes is insignificant, and in cold ones the saccharine contents are proportionably small.

Both these facts seem to indicate the conversion of tartaric acid into sugar, not so as to make it necessary that all sugar should be formed from tartaric acid, but

so that at least a portion of grape sugar might be formed from tartaric acid. This transformation, which is maintained by Liebig,\* has been supposed to affect the sweetening of the wine. All bottled wines which improve at all, become sweeter, and old wines always appear to have gained in sugar. The quantity of sugar cannot increase in weight, but it becomes more evident to the taste when tartaric acid is decomposed, and if the tartaric acid be converted into sugar, it furnishes an additional reason for the increased sweetness.

But this opinion loses all support when we remember that Bérard found † that although the acids in fruit diminished a little during ripening, such diminution was by no means proportioned to the increase of sugar. In some fruits, as cherries and pears, the acids increase, but the sugar increases still more in proportion.

Frémy ‡ is of opinion that a larger quantity of base saturates the acids in the fruit at the time of its ripening, but Crasso's experiments (p. 17) contradict this assertion. Schubert has tried to prove that the sweetening of wine proceeds from a separation of tartar, § but this separation cannot be perceived in bottles, and the change we are now discussing takes place in bottled wine. That wine in casks containing a great deal of

\* Journal de Pharm. tom. iv. p. 85, 1844.

† Phys. Scheikunde, p. 900.

‡ Journ. de Ch. Méd. Mars 1845, p. 132.

§ Pogg, Ann. Bd. 70.

cream of tartar, and little free tartaric acid, and constantly re-filled after evaporation, may become sweeter, is beyond a doubt, for water is evaporated, the alcohol increases, and as a necessary consequence, cream of tartar must be precipitated. Wines, therefore, which are rich in alcohol, possess much less tartar (since this salt is insoluble in alcohol), and on this account alone must be less acid. It still remains a question, what occurs in bottled wines which become less acid by keeping, and the alcoholic contents of which cannot be increased, since such sugar as is present in the wine needs ferment to set it in fermentation? And with regard to the sweet taste of cellared wines, the saccharine contents are not diminished. It is well known by Büchner's experiments,\* that acetate, citrate, and tartrate of potash in solution may be acted upon either by ferment or by other substances, and converted in a short time into carbonate of potash. The decomposition in which Büchner perceived this transformation was actual putrefaction, and cannot, therefore, be brought to bear upon what takes place in wine. I thought it right, however, to mention it here, since the same kind of results may as often be obtained from a slow process as from one which runs its course quickly, though under circumstances differing widely from each other.

If the free tartaric acid contained in wine were slowly converted into non-acid products, it would

\* Ann. der Ch. und Pharmacie, Bd. 78, s. 203.



alone be sufficient to render the wine sweet; the tartrate of potash would not require to be transformed into carbonate.

Lastly, it may be well to observe that tartaric acid dissolved in water contributes more than any other organic acid to the production of mould, and thereby induces the formation of cellulose; this explains the fact, that in test bottles the solution of tartaric acid requires frequent renewal. Cellulose, like sugar, is a substance containing C and HO, and therefore gum and vegetable mucus. It is, therefore, possible when wine has been long in cellar that among other changes tartaric acid may be converted into gum or vegetable mucus. We shall consider, in treating of the odoriferous constituents of wine, the important part played by tartaric acid in the improvement of cellared wine, and next to alcohol this acid may be looked upon as the most important constituent of wine.

Such wines as contain, in consequence of being cellared, less free tartaric acid (however the effect be produced), will, if red wine, become darker in colour as they sweeten, because a smaller proportion of free tartaric acid allows the blue colouring matter to become more evident.

I can treat better, in another place, of that thickening which is effected in wine by time, and renders it like syrup. I must here mention the unfavourable results of the cellaring of wine, particularly when it is

preserved in wooden casks, since many different properties of wines are, or may be, affected by this circumstance. The excellence of the wine is necessarily affected by the wood of the vessels in which it is preserved. Wine dealers have learned to understand and distinguish the effect produced in this manner upon the taste, colour, strength, and other qualities of wine, and Fauré\* has given us a detailed investigation. He pulverised the commonest kind of oak wood, exhausted it with ether, alcohol, and water, and obtained wax, quercin, quercitron (a yellow colouring matter), tannic acid, vegetable mucus, albuminous matter, gall-extract, and bitter extractive matter.

Quercin is a substance which, though easily soluble in alcohol and ether, is but sparingly so in water. It is found in all kinds of oak-wood, and cannot be entirely without influence upon the wine, since it has a peculiar odour.

If wine be put into oaken casks there will be an increase in the tannic acid, which already exists in it in larger or smaller quantities. But albumen is also present in the oak-wood, and as soon as the watery ingredients of the wine have dissolved the tannic acid, it will unite with the albuminous matter, and adhere to the wood.

Quercitron (the yellow colouring matter) is of importance if we would know the action of the wood of the casks in which wine is stored. Rigaud has ana-

\* *Agricult. Praticien*, 1852, p. 125.

lysed it.\* It is found in the *quercus tinctoria*, and is, therefore, only met with in American oaks. Rigaud found that quercitron =  $C^{36} H^{20} O^{21}$ , and can be resolved by the absorption of 2 H O, into  $C^{12} H^{12} O^{12}$  grape sugar, and  $C^{24} H^{10} O^{11}$  quercetin, a lemon-coloured powder destitute of taste and smell, and easily soluble in alcohol, though but sparingly so in water.

Quercetin is likewise easily dissolved in alcohol, and but sparingly soluble in water, destitute of odour, and has a weak bitter taste. As far as the properties of wine are concerned, colour excepted, it is of no value. Fauré tested the effect of oak-wood upon wine, brandy, and alcohol, by distilling the powder with these liquids for eight days consecutively. All three suffered alteration. Oak-wood from Dantzic and Stettin did not much affect the colour of the white wines of La Gironde, but a little dissolved quercin imparted to them a pleasant balsamic flavour. The same white wines when treated with oak-wood from Memel, Lubec, and Riga, were much coloured, and their taste was rendered so astringent by the dissolved tannic acid, that the flavour of the quercin could no longer be perceived. American oak has but little effect on the white wines of La Gironde, neither colour, taste, nor smell were much altered by it, though they acquired a certain bitterness which was only perceptible when powder was employed, not when the wine was brought into contact with whole

\* Ann. der Ch. u. Pharm. Bd. 90, s. 283.

pieces of oak. The Bosnian oak (from the shores of the Adriatic) affects white wine so strongly, by imparting to it a large portion of tannic acid, that exposure to the air will often turn such wine black. This wood is, therefore, not suited to wine-casks. French oak (from Angoumois) is less injurious, although it gives a good deal of tannic acid to the wine.

The case is different with red wines, which already contain a certain proportion of tannic acid, and whose quality cannot be much affected by a slight increase in this ingredient. The colouring matter of the wood is fixed by the colouring matter of the wine, but such of the constituents of the wood as impart flavour and odour may pass into the wine. Fauré does not approve of previously treating the wooden casks with alkalis, since alkalis render tannic acid darker; instead of this he recommends sulphuric acid with water ( $\frac{1}{6}$  sulphuric acid), to be left standing 24 hours, and the casks afterwards washed out with water. In considering the action of oak upon wine, we must distinguish between coloured and non-coloured wines. All light-coloured wines suffer greater or less alteration, and we shall speak more particularly about them in considering the colouring matter of wine.

We must also make a distinction between old and new casks. Old casks, which have already been used for the same purpose, have either entirely, or in great

degree, lost those substances which they could impart to wine; whilst new casks, unless they have been cleaned, impart a good deal. Hence it follows, that wines which spoil easily, on account of containing too much albuminous matter, may be materially improved by remaining for some time in new open casks; for the tannic acid of the cask either precipitates or renders inert the superfluous albuminous matter of the wine.

Old casks may, however, be injurious to wine on another account, namely, by decomposing such tartar as is deposited, or even by only rendering the tartar acid. In this case it is advisable to wash out the casks with *milk of lime*.

In order to preserve the wine from any such effect as may be produced by the casks, a custom has been introduced by the wine dealers of Burgundy, and has obtained now, for some years, of preserving the wine in walled-in reservoirs.\* The hard stones are cemented and coated with Roman cement. The trough is pumped full of water, which is then removed, and the reservoir dried before being filled with wine. This wine remained free from lime, and if we may trust the reports, improved just as much as in wooden casks. The reservoirs are furnished with an opening, and fastened with a wooden lid.

According to Stümcke,† the best means of pre-

\* *Moniteur Industr.* 1848, No. 1272.

† *Archiv. d. Pharm.* Bd. 70, s. 150.

paring casks for brandy which is to be exported colourless, is to fill them with water, and dissolve soda in it (3lb. to a hogshead), then conduct chlorine gas through it till it is present in excess, after which it may be let stand for eight days in the casks, which must afterwards be washed thoroughly with hot water. Doubtless the same method of cleansing might be applied to wine-casks. But as it occasions considerable expense, it would only be of real advantage in cases where the best wines were to be cellared or exported. All wines which have been long in bottle acquire a flavour which we ascribe to the cork. This is as great a mistake, as if we attributed the flavour of wine which has been long cellared to the cask.

The cause, in both cases, is fundamentally the same, though the accessory circumstances may differ. The moist cork, one side of which is in contact with the air, allows, equally with the wood of the wine-cask, the developement of mould plants. The taste and smell of wine is, under such circumstances, identical with that of many other mouldy substances, and is what we call musty. The mould of cork differs of course from that of wood, and the taste is consequently not exactly the same. The smell may be distinctly perceived in almost every warehouse in the country. The mould grows from the outside to the inside, and should it reach the inner side of the cask or cork it imparts a taste to the wine. On this account old wine casks must from time to time be

cleansed outside and inside, and new corks must be put into the bottles, even when the old ones are unhurt. If the inside of the cork be covered with rosin or sealing-wax, the entrance of air is cut off, and the formation of mould hindered, though not prevented.

Wines which have been long in bottle often acquire an unpleasant taste from this mouldiness; they are brought out to do honour to a guest, and praise is expected which cannot honestly be given.

It really seems strange that in this age, when so many other means can be employed, cork should still be made use of to stop bottles.

Poumier recommends, and Boullay and Chevallier are of the same opinion, that a small quantity of a fatty oil\* be stirred into the wine, in order to free it from the unpleasant smell it sometimes acquires from the cask. Many kinds of wine are improved by time and warmth, and cold in some cases imparts superior qualities to wine. Vergnette Lamotte, and Boussingault † have given us some statements respecting the manner in which the improvement of wine is effected by the action of cold. Lamotte, who tried experiments with Burgundy, observed, that the wine became turbid before the point at which ice melts was reached, and he found it deposited tartar, colouring matter, and a nitrogenous substance. Wine begins to solidify

\* Geiger's Mag. für Pharm. Bd. 27, s. 172.

† Bullétin de la Société d'Encouragement, 1848, p. 220.

partially some degrees below  $0^{\circ}$  ( $32^{\circ}$  F.), say  $10^{\circ}$  ( $50^{\circ}$  F.) or  $12^{\circ}$  C. ( $53.6$  F.). The ice formed consists principally of water, but contains some alcohol, and the wine which remains liquid becomes stronger. La-motte gives the following estimates of the alcoholic contents of the wine before and after freezing, and the amount of the ice which was separated.

		Alcohol before freezing.	Alcohol after freezing.	Deposit of ice per cent.
Red Burgundy, best kind	1837	11.5	12.1	12
"    "	1841	12.3	12.6	7
"    "	1842	12.7	13.1	7
"    ordinary	1844	10.5	11.0	8
White wine, best kind	1841	12.6	13.2	$7\frac{1}{2}$
"    "	1842	13.2	14.7	20

Now, as the best red Burgundy wines contain  $12\frac{1}{2}$ — $13\frac{1}{2}$  per cent. alcohol, and the white wines 13—15 per cent., freezing renders weaker wines almost equal to the better sorts in their alcoholic contents.

Boussingault has confirmed these statements by experiments made with other French wines.\*

But if cream of tartar be deposited as a result of the gradual effect of cold, this process, which is known

\* Ann. de Ch. et de Phys. 3rd série, tom v. p. 363.



by the name of stoney deposit, does not improve the flavour of wine. The crystals being once separated, are at best but imperfectly dissolved when the wine is again exposed to a warmer temperature, and the wine remains thick, an objectionable quality in such as is bottled.

It must be remembered that cream of tartar is a necessary ingredient in good wine, and the tartaric acid of this salt is one of the most important substances in wine. Wine which deposits stone does not improve by keeping nearly so well as wine which retains the cream of tartar in solution.

Vergnette Lamotte, and Boussingault make no mention of the flavour and other qualities of frozen wine, but confine themselves to the effect on the amount of alcohol; this, however, does not either principally or entirely determine the properties which render the flavour of wine agreeable.

## CHAPTER VI.

### DISEASES OF WINE.

UNDER this title we do not understand such alterations as are effected by time, and which may result in producing a less agreeable flavour. For many wines are improved, though the flavour of others is rendered less agreeable, and we must not expect that every change induced by time should be agreeable.

By the term "diseases of wine" is understood, strictly speaking, a condition in which the wine has become so altered and unfit for use, as to have lost its distinctive character. The diseases of wine have been classed under different heads, and we shall consider them in order.

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### THE TURNING OF WINE.

This disease shows itself under certain conditions of the weather, either suddenly, or in a very short time, and is peculiar to young wine. The colour of the wine becomes darker and its taste insipid. If the

disease increases, the colour becomes brown, the wine turbid, and of a disagreeable taste, and may at length disseminate fœtid gases and leave an acid liquid.

This disease is caused by a decomposition of tartar. That such decomposition takes place is known, but we are ignorant as to how it originates. Carbonate of potash is formèd out of cream of tartar, and so the colouring matter of the wine is altered and turned brown. In this manner the disease commences; it is then transmitted to the other constituents of wine, and eventually turns the alcohol into acetic acid.

Wine affected by this disease does not at first contain more acid than it did previously, since this disease differs from that which turns wine sour. The quantity of alcohol remains the same. The colour of the wine is first affected, and the taste becomes at the same time insipid and disagreeable. Batillat\* unjustly ascribes this disease to the decomposition of purpit, one of the colouring matters which he discovered in wine, and which consists partly of the colouring matter of wine, and partly of an apothema of tannic acid. Batillat's mistake consists in considering effect for cause.

In wine which is diseased in this manner, gelatine can no longer precipitate purpit, or apothema of tannic acid, since the acid tartar has been converted into alkaline carbonate of potash, which transforms both tannic acid and apothema of tannic acid into sub-

\* *Traité sur les Vins de la France*, p. 131.

stances which can no longer be precipitated by gelatine. The disease begins by resolving tartaric acid into carbonic acid. The addition of tartaric acid to the diseased wine does not restore the original colour to the wine, but makes it rose-coloured.

If the disease has not lasted too long, the quantity of alcohol continues the same as in good wine, and these diseased wines may, therefore, be used for the distilling and preparing of brandy. Every endeavour is made to remedy this disease, and render the wine saleable, by the use of alum and tartaric and sulphuric acid. French white wines of good quality are not subject to this disease; only the red wines are liable to it. The decomposition begins at the bottom of the cask, and is doubtless occasioned by the decomposition of the organic constituents of the wine ferment. It is here that the germ of the evil must be sought, for in these constituents is a substance which causes tartaric acid to decompose, and if aided by the air, oxidises it to carbonic acid and water. The wine cannot, therefore, become acid, for the carbonic acid either escapes, or combines with the potash of the cream of tartar.

The carbonate of potash thus formed changes the red colour into blue and brown, and causes decomposition in the tannic acid, and in the fatty acid compounds of the wine upon which its aroma depends. Experience teaches that sulphuric acid and alum, if used early enough, will prevent or arrest this disease.

But if it spreads, colour, flavour, and aroma are for ever gone, and the wine can be used only for distilling brandy: and it may proceed so far as to convert the alcohol into acetic acid, in which case putrid fermentation sets in.

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#### THE ROPINESS OF WINE.

This disease consists in the formation of vegetable mucus,  $C^{24} H^{19} O^{19}$ , from the sugar of the wine,  $C^{24} H^{24} O^{24}$ , water being at the same time separated. Vauquelin made this discovery.\* He received some bottles filled with the juice of the sugar-cane from Martinique. The juice was put into the bottles in the manner described by Appert; it was heated for a few minutes at a temperature of  $100^{\circ} C.$  ( $212^{\circ} F.$ ), and the bottles closed. The sugar was almost entirely converted into a tough mass, part of which had been deposited from the liquid, and was, therefore, not gum, and another portion was still dissolved. This flowed so slowly, that it could hardly be poured out of the bottle.

The same transformation may be remarked in beet-root, and in the juice of the carrot, onion, and many other plants; if they are exposed to a temperature of from  $30^{\circ}$  ( $86^{\circ} F.$ ) to  $40^{\circ}$  ( $104^{\circ} F.$ ), an escape of carbonic acid may be observed. Cane sugar is trans-

\* Ann. de Ch. et de Phys. tome xx. p. 93.

formed into grape sugar, and sugar disappears entirely when carbonic acid ceases to be resolved. Three substances in particular are thus produced—lactic acid, mannite, and vegetable mucus, but only a trace of alcohol. The lactic acid,  $C^6 H^5 O^5$ , and the vegetable mucus,  $C^{24} H^{19} O^{19}$ , are, together, equal to sugar minus water. The mannite,  $C^6 H^7 O^6$ , has 1 equivalent oxygen less than sugar, and this equivalent oxygen may have passed over to the albuminous matters of the vegetable juice, which consequently become oxidised.

According to Desfosses and Pélouze, this alteration, which is called mucus fermentation, may be produced at will by boiling beer ferment or gluten with water, dissolving sugar in it, and keeping it in a temperature of from  $30^\circ$  ( $80^\circ$  F.) to  $40^\circ$  ( $104^\circ$  F.).

Maclagan and Tilley\* have analysed the substance which is produced in ginger beer by this disease, and which is identical with that in wine. They found it to contain two equivalents of water more than vegetable mucus, namely—

		Eq.	Reckoned.
C. 43·9	43·8	24	43·7
H. 6·1	6·8	21	6·3
O. 50·0	49·9	21	50·0

This substance was insoluble in cold water, but swelled up very much when left in it.

As those wines which are subject to this disease are

\* Phil. Mag. vol. xviii. p. 12.

principally such as are deficient in tannic acid, a timely addition of this is recommended, as a preventive, by François.\*

No one can doubt but that tartaric acid has a great effect in causing the wine to become ropy. A solution of tartaric acid in water quickly becomes mouldy—that is, is converted into cellulose, the composition of which is analogous to that of vegetable mucus. (§ 84.) The alcohol of the wine protects the tartaric acid of the wine from spoiling—therefore, wines which are poor in alcohol, are more liable to the alteration of their tartaric acid. Sweet wines are more particularly liable to this disease, which sometimes disappears without the use of remedies, and sometimes may be removed by the addition of tartaric acid. François ascribes this ropiness to an excess of gluten (Dumas† and other French writers call it gliadine), although it is well known that Beccaria's gluten is gliadin and zymon.

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#### BITTERNESS OF WINE.

Burgundy wines are particularly exposed to this disease. The result is as if a second fermentation had taken place, inasmuch as a large quantity of carbonic acid is evolved.

\* Geiger, Mag. für Pharm. Bd. 33, s. 97.

† Chimie appliquée aux Arts, tome vi. p. 515.

The wine becoming bitter is ascribed to the formation of citric ether, which is very bitter. Whether or no this view be true, I cannot say.

This disease often disappears of itself; it is caused by the sediment; and hence, drawing off the wine into other casks will sometimes put a stop to it. Or young wine is added, which being rich in œnanthic ether, decomposes the citric ether.\* But where does the citric acid come from?

Tartrate of oxide of amyl is equally bitter. (See the Odoriferous Constituents of Wine).

Old Burgundy wines have mostly a somewhat bitter taste, which may be removed by mixing them with younger wines.

Batillat † recommends that first tartaric acid, and then bicarbonate of potash, should be mixed with the wine, and he says that he restored in this manner 8,800 gallons (400 hectolitres) of Burgundy, which had become bitter.

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#### THE ACIDIFYING OF THE WINE

depends upon the conversion of alcohol into acetic acid, and is, therefore, actual oxidation. This disease may be stopped at its commencement by adding carbonated alkali; but the colour of the wine will be

\* Schubert, *Techn. Chem.* Erlangen, 1854, s. 361.

† *Traité sur les Vins de la France*, p. 139.



lost, and the alkali imparts a disagreeable flavour to the wine. Weak wines are apt to turn acid if allowed to come in contact with air at a high temperature.

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#### THE MOULDINESS OF WINE.

This is a disease in which mould plants are produced on the surface of the wine. How this mould, which consists principally of cellulose, is formed, whether out of acetic acid which has been previously produced from the alcohol, or in any other manner, is not known. It is certain that the admission of air is favourable to this disease, and that alcohol disappears during its progress. This seems to indicate either that the alcohol is oxidised to acetic acid,  $C^4 H^6 O^2 + O^4 = C^4 H^4 O^4 + 2HO$ , which acetic acid then becomes cellulose,  $6 C^4 H^4 O^4 = C^{24} H^{21} O^{21} + 3HO$ , or that the alcohol is at once converted into cellulose, which, however, is very improbable.

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Greek wines are at present, generally speaking, bad, and spoil very easily. Landerer\* ascribes this principally to their being badly prepared, and imperfectly cleared; enough, they are turbid. In order to prevent them from becoming acid, which they do very easily, pitch and gypsum are added to them, and

\* Arch. der Pharm. Bd. 70, s. 292.

hence they are often called pitch wines. They possess so little alcohol that they are scarcely available for the manufacture of vinegar. One cause of their being so easily spoiled may be thus explained, since alcohol prevents chemical alterations, and weak wines spoil easily.

The addition of pitch and tar to the wines is no modern invention, for the ancients often drank wine prepared in this manner. They made use of pitch and tar in order that the combustible oil contained in them (creosote, &c.) might hinder chemical decomposition from taking place in the wine.

Such adulterations do not, however, prove that all the wines which need them were originally weak; for turbid wines, when they are not protected from the air, are equally liable to spoil quickly.

Whatever the disease of wine may be, the cause is always to be found in substances which are contained in the wine, and which can decompose themselves, and cause decomposition in others. There is no occasion to seek further if we find a certain quantity of that substance which has converted the sweet juice into wine, and a portion of which remains in the wine. An albuminous substance is to be found in all wines, which under certain circumstances causes the wine to become diseased, and occasions a variety of diseases according to the difference of circumstances. As a rule, the wine is improved by this albumen, which developes out of other bodies odori-

ferous and well-flavoured substances. Albuminous bodies are the causes of movement in the organic kingdom, active in the origin as in the decay of bodies, in the living plant as in its products. They have no repose till they are annihilated; and other substances, either to their advantage or disadvantage, are dragged into annihilation with them.

## CHAPTER VII.

### CONSTITUENTS OF WINE.

WINE may be divided into the following kinds:—

1. Sweet or liqueur-wines. Some of these have no excess of sugar; as, for instance, Madeira; others are enriched with sugar by the method employed in preparing them, which we have considered already (p. 51), and others again are prepared from dried grapes, or from evaporating a portion of the must—such as Malaga, Tokay.

2. Acid, or harsh wines. They are rich in tartaric acid, but poor in sugar. Rhine and Moselle wine.

3. Spirituous wines, Portuguese and Burgundy.

4. Wines containing tannic acid, to which most French wines belong. Except as containing less alcohol, they resemble the last.

5. Effervescing wines. Champagne and others.

In liqueur-wines the excess of sugar, which characterises them, may have been derived either from the grapes having contained too little albumen to set all the sugar in fermentation, or because so large a quantity of alcohol was evolved as to hinder the further action of the ferment, which then coagu-

lates, and is precipitated. By drying the grapes, or evaporating a portion of the must, sweet wines may be prepared from all kinds of grapes, and a richness in alcoholic or saccharine contents may be imparted to them, which they did not derive from the grapes. For this purpose grape juice ought to contain 50 per cent. sugar, and this it does not (p. 31).

As a general rule, harsh wines have most bouquet, that is, supposing them to be good, and not poor in alcohol and sugar. Spirituous wines, more especially heavy, loaded red wines, are apt to undergo in the course of time a considerable change in colour and flavour.

Such as contain tannic acid are also considerably affected by time, and lose their flavour.

Effervescing wines generally remain good only for a short time, since they are saturated with carbonic acid condensed in the wine. Since the preparation of effervescing wines needs scarcely any chemical explanation, we have not dwelt particularly upon it. The sweet fresh wine still in a state of fermentation is drawn off from the casks in which it would continue to ferment, and at once bottled. Fermentation still continues, and ferment is deposited, and in order to ensure its being deposited against the cork, the bottles are placed with the necks down. The corks are withdrawn and replaced by others, and this proceeding is continued till the wine remains clear. But fermentation has not yet quite ceased, on the contrary, sufficient carbonic

acid is evolved to saturate the wine, and produce tension enough to eject the cork the moment the string is cut, and cause the wine, which contains several times its own volume of carbonic acid, to pour foaming out.

Effervescing wine may be prepared from every good kind of grape juice.

An approximation to the composition of wine may be deduced from the general statement of the composition of grape juice given (p. 5), and from the change which it undergoes during fermentation, whether or no the skins are allowed to ferment. The composition differs according as the wine is red, or not red. In the last-mentioned, no particular colouring matters are found, and only a trace of tannic acid; in the former both are present. Alcohol and water are also among the principal ingredients, then sugar, gum, extractive and albuminous matters; then free acids, such as tartaric, racemic, malic and acetic acid, tartrate of potash, of lime, and of magnesia, sulphate of potash, common salt, and traces of phosphate of lime; also, and especially in cellared wines, substances which impart aroma, as *œnanthic* and acetic ether, in variable proportions, and other volatile matters of which we shall hereafter speak more particularly. In red wines and in many others, a little iron, and according to the statement given (p. 26), some alumina may also be detected. Lastly, the best wines contain, according to Fauré, a peculiar substance which he calls *œnanthine*.

These ingredients vary exceedingly in proportion. The quantity of some is so insignificant, that the substance almost disappears during analysis. The quantity of some may be determined by weight, and of others again is still greater. Most of the properties of wine depend upon the sugar, alcohol, tartaric acid, and water, which exist together in it; that is, putting aside taste and smell as standards of comparison. In every case they are the chief constituents. We will now examine each of these bodies particularly, trace its effect upon the excellence of the wine, and point out the methods by which it may be detected, and its quantity determined.

## CHAPTER VIII.

### THE AMOUNT OF ALCOHOL IN WINE.

WINE obtains its distinctive characteristics in the first instance from the alcohol, which exists in every kind of wine. The alcohol is the product of the fermentation of the sugar in the grape juice, that is, of grape and fruit sugar. The quantity of alcohol produced in the wine must always be in exact proportion to the quantity of sugar contained in the grapes. The sweet flavour of the grapes is not a test, for the genuine flavour may be masked by a large quantity of acid cream of tartar, so that grapes containing a great deal of saccharine matter need not necessarily be distinguished by their peculiarly sweet taste.

But the amount of alcohol in wine is not entirely determined by the amount of sugar in the grapes. Ferment is necessary in order to convert sugar into alcohol, a certain proportion of ferment to a fixed amount of sugar. The ferment is engendered out of the albuminous matters which exist in the grape juice, and upon these, therefore, the quantity of alcohol partially depends.

Three cases may here be considered,—



Either the amount of sugar exceeds that of the albuminous matter which is to be converted into sugar, and then the wine remains sweet after fermentation, since it still contains undecomposed sugar.

Or, the proportion of albumen to be resolved into ferment is greater, and then nearly the whole of the sugar will be decomposed, and the wine will remain slightly acid.

Or, the quantity of sugar and of substances convertible into ferment are equal, in which case the wine retains something of each, and is not acid.

Liqueur-wines exemplify the first, Rhine wine the second, and Burgundy the third.

But a still greater distinction must be made. Where much sugar, and a large quantity of the substances from which ferment are formed are present, the wine will be strong and rich in the amount of alcohol; when less of these substances exist, the wine will be proportionably less strong, and it will be weak if only a small quantity of either be present.

The opinion that wines containing a great deal of alcohol must necessarily be also sweet, has been decidedly contradicted, it being asserted that they do not contain a sufficient amount of the constituents of ferment to resolve all their sugar into alcohol and carbonic acid. But there is another point to be considered here. Even when sugar and ferment are present in sufficient quantities, it is not possible by means of fermentation to produce an alcoholic liquid

of any strength that may be wished. When a certain amount of alcohol has been produced, the further activity of the ferment is hindered by it even when an excess of sugar is still present.

This is the case with wines which contain more than 20 per cent. by volume of pure or absolute alcohol, that is to say, when the liquid has become too rich in alcohol, so that the fermenting matters coagulate, and become insoluble, and therefore inert. Experience teaches us, therefore, that if the amount of alcohol has during fermentation fully reached to 20 per cent. by volume, this may be considered as a maximum, after which fermentation is impossible. All sugar which is still left remains undecomposed, since the ferment has lost the power of exciting fermentation in the strong alcoholic liquid.

There are also substances in wine which oppose fermentation, and these, even when sugar still exists, may prevent a portion of the albumen from being converted into ferment, and acting as such. Albuminous matter and sugar are therefore to be found in all wines. The substances which principally oppose fermentation are acids, and the tartrate and malate of potash, when present in excess. If, for instance, the grape juice contains too much cream of tartar, this will hinder fermentation by rendering a portion of albuminous matter inert, and thus causing some of the sugar to remain undecomposed. A certain quantity of acid or super-salts is of use; too

much is injurious. Besides this, tannic acid appears to check fermentation. If the quantity of these acids be too great, the albuminous matter will be too much checked to allow of its conversion into ferment, and a proportionate quantity of sugar will remain undecomposed.

Lastly, we must not overlook the fact that even when the composition of the grape juice is such as favours the formation of alcohol, its amount, which depends upon the maintenance of satisfactory fermentation, must be considerably affected by the weather, as also by the temperature and other external circumstances.

There are many interesting circumstances connected with these facts with which we would gladly be acquainted, but which must be the subject of future investigation. It is well known, for example, that fermentation takes place as well during the formation as during the decomposition of ferment, and that consequently during the fermentation of grape juice and the production of alcohol, the two points must be kept distinct, namely—fermentation during formation, and during decomposition of yeast. But, although we know that such a difference does exist, the conditions which govern it have never yet been made the subject of research. The influences which might check the formation of yeast differ, at least partially, from those which hinder its decomposition. The formation of ferment is in every case affected by the

quantity of the substance of which the walls of the ferment cells are composed, and it is decidedly influenced by the quantity of gum existing in the grape juice. If during the development of the grapes but a small portion of gum has been formed in them, fermentation will certainly ensue, since albuminous matter is of itself sufficient to cause fermentation, without being converted into ferment, as is the case with fibrin, gelatine, &c.; but the fermentation will differ essentially from that in which ferment cells are normally engendered in sufficient quantities; for which purpose it is not necessary that any portion of sugar should be expended. (P. 64.)

That the formation of ferment is affected by the weather in a different manner from its decomposition is known, but who can explain the difference? We are acquainted with the varieties occasioned by an unequal admission of air. (Pp. 55 to 60.)

I have only been able to take a superficial view of the many circumstances which affect the production of a larger or smaller quantity of alcohol, and which must be considered if any one wishes to form a general idea of the causes upon which the variations in the amount of alcohol in different wines depend.

As yet only a few of these circumstances can be fully explained; with respect to many others we know that they exist without being able to account for them, and we are quite in the dark as to many of those properties of wine which, though intimately

connected with the formation of alcohol (in so far at least as their origin from alcohol is concerned), cannot be derived from the alcohol which is actually present in wine. If we confine ourselves to a general statement we may say that in Rhine wines, among which, in spite of many varieties, a general resemblance may be found, the original quantity of alcohol is less than in Madeira wine; these two kinds of wine differ considerably. A generic connexion between the peculiar qualities of Rhine wine and the small amount of alcohol is as undeniable as that between the peculiarities of Madeira and the larger alcoholic contents.

In general, it may be considered as a fact, that in wines which contain an abundance of alcohol a large amount of albumen and sugar may be supposed to have existed in the grape juice, and more flavour and aroma is possessed by such wines than by those which are weaker. I say, in general; for there are many exceptions to this rule, and its real value is generally clearly understood; thus the more albuminous matter and sugar are contained in the grape juice, the more perfect will be the development of the fruit, and the greater the facility with which other substances may be developed in it.

We may observe with respect to the alcoholic contents of effervescing wines, that they contain somewhat more alcohol at the time when they are poured out than they did a short time before. In the fermentation which immediately precedes their use, a

little sugar is decomposed, and a little ferment formed; thus after a few seconds the clear wine becomes more or less thick—this is often the case with champagne.

With respect to the alcohol of wine, it is no longer necessary to put the question which in the time of Fabroni was answered in the negative—namely, whether alcohol (as such) was found in wine? one of the reasons given among others for denying it being that when spirit distilled from wine was added to it again, the flavour of the liquid was altered. Alcohol is obtained from wine by distillation, and it contains a portion of the water from the wine, and of such volatile substances as are contained in wine. The latter are known under the common name of fusel oil; this is best removed by renewed distillation with animal charcoal, the alcohol is obtained anhydrous by repeated distillation with unslacked lime. The alcohol purified in this manner is exactly the same, from whatever kind of wine it may be obtained.

The composition of wine can be as little determined by its specific weight, as the value of any other liquid, be it milk, beer, vinegar, &c., can be so decided. Substances heavier than water are found in wine, such as sugar, salts, &c., besides alcohol, which is lighter than water. The specific weight of such a mixed liquid depends on the kind and quantity of the first-mentioned ingredients, and on the amount of alcohol contained in it.

The simplest method of ascertaining the quantity of alcohol contained in wine is to distil the spirit from the wine, determine its specific gravity and quantity, and compare it with the quantity of wine which has been employed.

Various instruments have been constructed to effect this purpose, and one small apparatus was arranged by Gay-Lussac; but the simplest apparatus which can be used is a retort, with a tubular refrigerator (consisting of a glass tube fixed in the centre of a tin jar, so that it may be kept filled with cold water). The tube must be bent at a right angle, and terminate in a cylindrical measure-glass, shaped like a bottle, divided into cubic centimetres, and be kept sufficiently cool. Care must be taken to prevent the alcohol from evaporating, as also that the apparatus be securely closed, and everything except the retort be kept cool.

Of course one of the first things to be considered is, how much of the wine should be distilled over. Some content themselves with one-third, and determine the alcoholic contents from that. If, for instance, in the distillate 33 parts out of 100 are composed of alcohol, the quantity of alcohol in the wine will be 11 per cent. for  $\frac{33}{3} = 11$ .

It is, however, advisable to distil over more than a third, especially in the case of strong wines, and when a glass retort and water bath are used in distilling. If the wine does not boil, the alcohol evaporates more slowly. I consider it better in general to allow

distillation to continue till at least half is distilled over. If the density of the liquid which has been distilled is such as to give 25 per cent. alcohol at the above-mentioned temperature, then 25 divided by 2 gives the alcoholic contents of the wine at  $12\frac{1}{2}$  per cent.

The bottle-shaped cylinder measuring-glass may be dispensed with, for if 100 parts of 200 cubic centimetres of wine be distilled, and sufficient water be added to it after distillation is over to make it again 200 C. C., the specific gravity of this liquid will, at a uniform temperature, give the exact alcoholic contents of the wine. This last process is not, however, advisable in the case of weak wines, or when the areometer is to be employed, to determine the density, as it is less easy to read it accurately when the liquid is very watery than when it contains more alcohol.

Simple as this method of determining the quantity of alcohol is, one still simpler has been sought. And perhaps when many kinds of wine are to be examined, a method by which the result desired may be more speedily attained is necessary. For this purpose an instrument has been recommended which, though differently put together by Brossard-Vidal, Conaty, and Lerebours, is nevertheless founded on the same principle.

Alcohol boils at a low temperature, water at a higher, a mixture of alcohol and water always at a lower temperature than water alone, and that in



proportion to the quantity of alcohol. A thermometer tube is made use of, filled with quicksilver in such a manner as to show all the varieties of temperature between boiling water and a boiling mixture of 75 parts water and 25 parts absolute alcohol. Then let the following mixtures be made—95 parts water and 5 parts alcohol; 90 water and 10 alcohol; 85 water and 15 alcohol; 80 water and 20 alcohol; 75 water and 25 alcohol. Let water be boiled in a copper vessel at a pressure of 760 millimeters (29.9 inches), and the above-mentioned thermometer tube be placed in it, and the part to which the extreme point of the column of quicksilver reaches must be marked 0. The thermometer tube being again placed in the vessel, the mixture of 95 parts water and 5 parts alcohol must then be boiled, and the end of the column of quicksilver then be marked with 5. The same process must be repeated with the mixture of 90 parts water and 10 alcohol, and the tube marked 10; 15 at the point to which the quicksilver mounts in a boiling mixture of 85 parts water and 15 alcohol; 20 in that of 80 parts water and 20 alcohol, and 25 in 75 parts water and 25 alcohol. The space between 0, 5, 10, 15, 20, 25 may be equally divided. The scale upon which the degrees are marked, must be connected with the tube in such a manner as to be moveable, and capable of being turned by a screw in either direction, so that in every experiment where the atmospheric pressure is different, the thermometer may be first dipped in boiling water,

and the 0 of the scale placed exactly level with the end of the column of mercury. In this manner the instrument may be used to test wine.

In order to determine the alcoholic contents of wine, the thermometer (ebullioscope) should be dipped into wine which is in a copper vessel, and then it should be made to boil quickly. The point which the mercury attains in the thermometer tube, gives directly the amount of the alcohol. If this should reach the division 15, then 15 per cent. absolute alcohol exists in the wine.

It will easily be understood that success depends upon two points. First, that the solid matters which exist in wine do not perceptibly raise the boiling point (that is, not during the experiment); and secondly, that when the wine begins to warm, and before it boils, as much alcohol and water is evaporated as during the experiment, which originally served for graduating the tube. I will experimentally examine both points. It is necessary to be very watchful and quick whilst graduating the instrument, and whilst examining any wine, in noticing the height of the mercury. It is reckoned that half a minute may elapse, and that the temperature of wine containing 15 per cent. alcohol, and of a mixture of 15 parts alcohol and 85 parts water, may remain stationary for a minute. If the first half minute be allowed to pass, the experiment must be repeated with another liquid, since in that case too much alcohol evaporates, and the experiment becomes

valueless. It is also necessary that this experiment with wine should be made in a vessel of the same shape and metal as that in which the thermometer was graduated; further, that the bulb of the thermometer (ebullioscope) must be placed in the middle of the fluid, and attention must likewise be paid to everything that tends to promote equable boiling.

One great difficulty here is how best to apply heat. If it be irregularly conducted, now quickly and then slowly, it would in the latter case cause relatively more alcohol than water to evaporate before the liquid boiled, and that is the moment for observation, and the alcoholic contents of the wine would then be estimated too low. A uniform source of heat, which will cause the liquid to boil quickly, is therefore absolutely necessary.

That alcohol evaporates before the liquid boils is certain, and this occurs in the same manner in the experiment which serves to graduate the thermometer, as when the instrument is made use of to analyse wine.

The points which I have endeavoured to investigate are, first, whether the evaporation from alcohol before the liquid boils, and when boiling begins, be as great in wine as it is in alcohol and water; and secondly, whether the solid constituents of wine do not so modify the boiling temperature as to render the instrument inaccurate. It is scarcely necessary to remind the reader that its applicability must depend upon these details.

The first point was easily examined. 20 cubic centimetres of red wine, which contained 10·5 per cent. alcohol was poured into a flask, and into another flask of equal size water with 10·5 absolute alcohol was put, a liquid therefore containing the same amount of alcohol as existed in the wine. Thermometers were then placed in these flasks, and the whole were weighed. They were then plunged simultaneously into an oil bath, in which the temperature was rising. The wine in the one flask boiled 10 seconds before the alcohol and water in the other. After both had remained at boiling point one minute they were immediately cooled and weighed.

The loss in 20 cubic centimetres wine was 1·268

Ditto in alcohol and water . . . . . 1·280

Therefore in 20 CC, (that is, 19·5 grammes (300 grs.) for the spirit, and 19·9 (306 grs.) for the wine), a difference of 0·012, which gives a difference of six parts by weight in 10000.

This difference may, however, be neglected, if exactly the same method of heating be employed, and the same amount of time be used in bringing the water to a boiling point, it being never allowed to remain boiling more than a minute. I am now only speaking of wine which, like that employed in this experiment, contains 1·64 per cent. extract.

It was necessary to examine the effect produced upon the boiling temperature by the solid constituents held in solution by wine. The quantity of solid con-

stituents varies from 1 to 25 per cent., and more, it varies in different kinds of wine, and it is not necessary to examine whether water, with 25 per cent. sugar, cream of tartar, &c., boils at a different temperature from pure water, for this is well known, but whether the difference between the boiling points be sufficient to render the ebullioscope useless. And unless it give the alcoholic contents within 1 per cent., it must certainly be considered useless.

We shall see further that the specific gravity of wine the alcohol of which has evaporated, and the original volume of which has been replaced by water, varies between 1.0083, the residue of Rhine wine, and 1.1030, the residue of white Bergerac. At what temperature does such a liquid boil? By examining this point we shall be able at once to determine the influence exerted upon the boiling point by the solid constituents of wine.

The following are the results which have been obtained—water boils at 210.65 F. 99° 25 C. or at 211.55 F. 99° 75 C. if boiled speedily in a platinum vessel. And Burgundy-Pommard freed by distillation from alcohol, and reduced again to its original volume, boiled at the same time in the same platinum vessel at 212 F. 100° C., and boiled more strongly at 212.9 F. 100° 5 C.; the wine, after evaporation, left 1.80 per cent. extract.

Roussillon wine, treated in the same manner, boiled at 211.75 F. 99° 75 C. and more strongly at 212.45 F. 100° 25 C. The wine gave 2.87 extract. White Ber-

gerac boiled at 215·6 F. 102° C., and more strongly at 216·5 F. 102° 5 C. The wine gave 26·81 extract.

Nothing more can be required for the rejection of this method. The experiments made were scarcely necessary, since it is sufficiently known that no constant temperature can be maintained in any boiling liquid, water not excepted. Pure water put into a glass vessel boiled at 217·4 F. 103° C. At the same time, when placed in a platinum vessel, it boiled at 211·55 F. 99° 75 C. And a thermometer in the fluid rises and falls according as more or less hot vapour rises from the bottom of the vessel.

For this reason the scale of the thermometer is not graduated by placing the bulb in boiling water, but by exposing it to the steam.

Those who maintain that the temperature of boiling water in a vessel can be determined within half a degree, have either never watched the process of boiling closely enough, or have not used the thermometer sufficiently.

But another source of inaccuracy is found in the solid matters of wine. Let us take the highest temperature both of water and of wine without alcohol, after it has been reduced by water to its original volume.

The water boiled at 211·55 F. 99° 75 C.

Wine, with 1·80 extract, at 212·9 F. 100° 5 C.

„ 2·87 „ 212·45 F. 100° 25 C.

„ 26·81 „ 216·5 F. 102° 5 C.

Each of these temperatures is higher than given by water, in consequence of the fixed ingredients which remain in wine when freed from alcohol. But if these solid matters raise the boiling point of wine which has been freed from alcohol and restored to its original volume by the addition of water, they must have the same effect upon wine in which alcohol still exists.

Fixed ingredients in wine raise the boiling point; the alcoholic contents, if deducted from it, will be estimated too low, and that in proportion to the amount of the extractive matter.

Pohl,\* like Gröning and Brossard-Vidal, has made use of the ebullioscope, and, according to him, even 15 per cent. sugar has no effect upon the boiling point of water; and a mixture of 10 parts alcohol, 15 parts sugar, and 75 parts water, boils at the same temperature as a mixture of 10 parts alcohol, and 90 parts water. We learn from his statements that a mixture of alcohol and water, when it first boils only remains stationary at a fixed point for a short time, it then rises gradually a little, and afterwards (supposing the liquid mixture to contain 146 grammes, (2253 grains)) remains at a fixed temperature for from 4 to 16 seconds. It is in this last period, during which the thermometer remains stationary, that Pohl gives us the weight per cent., of alcohol in the mixture, at 760 millimetres. (29.9 inches) barometric pressure.

\* Liebig and Kopp, Jahresber, 1850, s. 455.

Absolute Alcohol.	Temperature.	
0 . . . .	212° F.	100° C.
1 . . . .	209·82	98·79
2 . . . .	208·07	97·82
3 . . . .	206·33	96·85
4 . . . .	204·60	95·90
5 . . . .	203·03	95·02
6 . . . .	201·57	94·21
7 . . . .	200·17	93·43
8 . . . .	199·00	92·78
9 . . . .	197·65	92·03
10 . . . .	196·50	91·40
11 . . . .	195·49	90·83
12 . . . .	194·48	90·27

But how was Pohl able to determine the temperature to the second decimal point?

At the same time at which the results given (pp. 151, 152) were obtained, wine was boiled in the platinum vessel in the manner there described. It was Bordeaux wine, containing 1·64 per cent. extract, and 10·5 per cent. alcohol. The thermometer stood at 197·6 F. 92° C. when boiling was first clearly perceptible, but it was at 199·4 F. 93° C. before the wine could be actually said to boil. As the highest boiling point of water was at the same time 211·55 F. 99° 75 C. 199·4 F. 93° C. is perhaps too low. But call it 199·4 F. 93° C. or even 197·6 F. 92° C.

According to Pohl this would prove 9 per cent. alcohol to be in the wine, and analysis gives 10·5 per cent. alcohol.

Spirit of exactly the same strength, namely, 10·5 per cent. by volume of alcohol was made; although it



was superfluous, its specific gravity was taken ; it gave exactly 10·5 per cent. alcohol. This spirit in the same platinum vessel gave the first sign of boiling at 197·6 F. 92° C. and boiled completely at 199·4 F. 93°C.

These are the same temperatures at which wine containing 10·5 alcohol, and 1·64 per cent. extract boiled. So far one might imagine the ebullioscope could be trusted. But then we overlook the uncertainty of a whole degree in the temperature in the first place, and secondly, the effect of the solid matters of the wine, which amounts here to half a degree, and might, in wines containing a great deal of sugar, rise to  $2\frac{1}{2}$  degrees C. =  $8\frac{1}{2}$  degrees F.

For these reasons I have been led to consider the ebullioscope as useless in cases where accuracy is required.

Silbermann has made use of another method of ascertaining the alcoholic contents of wine. He starts from the point that heat renders alcohol much more elastic than water, and makes use of an instrument for determining the quantity of alcohol, the construction of which we will describe as simply as possible. A thermometer tube with a bulb is filled with water, and dipped into a liquid warmed to 77 F. 25° C.; the point at which the water in the tube stands is marked, the liquid warmed to 122 F. 50° C., and the point to which the water then rises likewise marked. Then let the apparatus be filled

with pure alcohol, so that at a heat of 77 F. 25° C. the alcohol should stand at the lowest point before attained by the water. If the instrument be now dipped into a medium of 122 F. 50 C., the alcohol being three times as much expanded by the heat, will stand higher than the water did at 122 F. 50 C. The interval between the point reached by the water and that attained by the alcohol at a temperature of 122 F. 50° C., must be divided into 100 equal parts. If the instrument be now filled with wine to the point which the water reached at 77 F. 25 C., and the apparatus warmed to 122 F. 50 C., the wine will rise in the tube just in proportion to the amount of alcohol it contains.

The use of this instrument assumes that the non-volatile constituents of wine (sugar, &c.) do not interfere with the expansion of the liquid. I shall pass over in silence the easiest manner of arranging and filling this instrument.

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The halymetric method of analysing the alcoholic contents of wine was first tried by Fuchs upon beer, and afterwards by Zierl upon wine. Pure powdered common salt is taken and divided into fixed quantities, one portion is dissolved in pure water, another in any liquid that may be chosen; another in wine, which dissolves less in proportion to the amount of

alcohol, and another portion in wine which has been boiled down, and restored by water to its original volume, and in this the amount of salt dissolved is less in proportion to the foreign substances dissolved in the boiled wine.

By examining how much salt is dissolved in wine, and how much in wine that has been boiled and restored to its original volume, we may determine approximately the extractive and alcoholic contents of the wine. The method is, however, very imperfect.

There is another means of determining the alcoholic contents of wine, which especially recommends itself on account of its simplicity. It is employed by Tabarié, and may be applied to beer as well as to liqueurs, and other spirituous liquors. The specific gravity of the wine to be tested is ascertained, half its volume is evaporated in the open air, sufficient water is then added to the remainder to restore its original volume, and the specific weight is again determined. Tabarié has constructed a peculiar areometer for determining specific gravities, and called it an œnometer. It is not necessary to dwell upon this subject, but we may just observe that an areometer which exhibits densities ranging from 0.990 and 1.104, having therefore 114 divisions, is sufficient for any kind of wines, for there is no wine of less specific gravity than 0.990, and none of greater specific gravity when freed from alcohol, and again diluted with water than 1.104.

It is useless to take three decimal points, for the observations cannot be made accurately.

The principle upon which this method rests is simply this, alcohol decreases, and non-volatile substances increase the specific gravity of wine. If the alcohol be allowed to evaporate, its quantity must be determined, as far as may be, by ascertaining the difference between the specific gravity of the wine and that of the residue to which water has been added.

It is self-evident that even this method cannot be absolutely accurate, since the solid constituents are differently circumstanced in wine, according as alcohol is present or non-present. The only question of importance here is, whether the method be serviceable; that is, whether the strength of the wine can be determined by it with sufficient accuracy. Experience has taught me that it is applicable, and I have no hesitation in preferring it to every other method, when a large number of wines are to be examined. It is only necessary to measure off a certain quantity of wine with a pipette, the contents of which are known, and to ascertain its temperature and specific gravity (which can be done, if preferred, by an areometer), then place this wine in an open glass in a water-bath, till about half has evaporated; water must then be added to it till its original volume is restored; it must be reduced again to its original temperature, and its specific gravity ascertained, thence the alcoholic contents of the wine can be learned. And indeed the

whole examination (if we except the evaporation, which need not be reckoned exactly according to time) may be completed by the use of the areometer in the course of a few minutes. The result is almost as accurate as that obtained by distilling wine, and ascertaining the specific gravity of the distilled liquor. In using this method it is necessary to allow for the difference which exists between the specific gravity of wine which has been evaporated and restored to its volume, and the specific gravity of the wine originally, by subtracting the one from the other. The difference then gives the specific gravity of the alcohol and water as they exist together in wine.

Suppose that at  $10^{\circ}$  C.  $50^{\circ}$  F. the specific gravity of wine =  $0.9953$ , and that of wine freed from alcohol and restored by means of water to its original volume =  $1.0080$ , subtract  $0.0080$  from  $0.9953$ , and the remainder =  $0.9873$ . Spirit having a specific gravity of  $0.9873$ , at  $50^{\circ}$  F.  $10^{\circ}$  C., expresses  $9\frac{1}{2}$  per cent. absolute alcohol, at  $59.5$  F. and  $15^{\circ} 5$  C. which is therefore the alcoholic contents of the wine.\*

The following experiments, made at a temperature between  $9^{\circ}$  and  $10^{\circ}$  C.  $48.2^{\circ}$  and  $50^{\circ}$  F., have convinced me more especially of the peculiar suitableness of this method.

Red Bordeaux has a specific gravity =  $0.9951$ . 200 CC were distilled in a retort to 100 (as explained,

\* In all these determinations I have followed Tralles, whose statements may be found in Gerhardt, *Traité de Ch. organ.* tom. ii. p. 258.

p. 145). The spirit which passed over, being diluted with water to 200 CC., had a specific gravity = 0.9858. The wine remaining in the retort, when re-diluted with water to 200 CC., had a specific gravity = 1.0089. Specific gravity of wine 0.9951, minus 0.0089 = 0.9862. 0.9862 gives 10.3 per cent. absolute alcohol, whilst the specific gravity of the spirit which was distilled over = 0.9858, and this gives at 95.5 F. 15° 5 C. 10.6 per cent. alcohol.

Thus Bordeaux wine contained 10.5 per cent. alcohol by volume, showing a difference of  $\frac{1}{3}$  per cent.

The experiment was repeated upon the following wines—

Port wine, specific gravity = 0.9970.

Spirit distilled from it, and restored by the addition of water to its original volume = 0.9763.

The specific gravity of the wine, freed from alcohol, and diluted by water to its original volume = 1.0205.

9970 — 0.0205 = 0.9765, which, at a temperature of from 48.2 F. 9 C. to 50 F. 10 C. (at which all these experiments were made), gives 20 per cent. alcohol in the wine, whilst 0.9763, the ascertained specific gravity of the spirit, gives  $20\frac{1}{4}$  per cent. alcohol. Here, then, is a difference of  $\frac{1}{4}$  per cent., which, however, in experiments of this kind may be safely disregarded.\*

\* I may here observe that the determinations of sp. gr. all through this treatise were made by weighing a glass pear, a description of which is given in the investigation of sea water (Scheik. Onderz. deel. 6, p. 1,) and the weighings were made with a balance which was sensitive to 0.1 milligramme (0.015 grain).

Madeira, specific gravity = 0.9971.

Spirit distilled from it, and restored again by water to its original volume, has a specific gravity of 0.9782. The wine freed from alcohol, and reduced to its original volume by water, has a specific gravity = 1.0181.  $0.9971 - 0.0181 = 0.9790$ , gives at 59.5 F., 15°, 5 C.  $17\frac{1}{3}$  per cent. alcohol, whilst 0.9782, the specific gravity of the wine, would give 18 per cent. alcohol. Here, again, is a difference, as the spirit distilled over showed a higher rate of alcohol.

Teneriffe wine, specific gravity = 0.9945.

Spirit distilled (as above), specific gravity = 0.9790.

Wine, evaporated in the manner detailed above, sp. gr. = 1.0151.  $0.9945 - 0.0151 = 0.9794$ , which gives exactly 17 per cent. alcohol, whilst the specific gravity of the spirit, which was found to be 0.9790, gives the alcoholic contents of the wine at  $17\frac{1}{3}$  per cent.

Rhine wine (Rüdesheimer) . sp. gr. = 0.9960

Spirit, as detailed above . . sp. gr. = 0.9881

Evaporated wine . . . . sp. gr. = 1.0086

$0.9960 - 0.0086 = 0.9874$ , representing alcoholic contents =  $9\frac{1}{3}$  per cent., whilst 0.9881 the specific gravity of the distilled spirit, gives  $8\frac{2}{3}$ , that is, a difference of  $\frac{2}{3}$  per cent. in the alcoholic contents.

Let us now compare these results.

	Alcoholic contents of evaporated wine.	Alcoholic contents of Spirit.	Difference.
Bordeaux ....	$10\frac{2}{3}$ per c.	$10\frac{1}{2}$ per c.	$\frac{1}{3}$ per cent.
Port Wine ....	20	$20\frac{1}{4}$	$\frac{1}{4}$
Madeira .....	$17\frac{1}{3}$	18	$\frac{1}{3}$
Teneriffe ....	17	$17\frac{1}{3}$	$\frac{1}{3}$
Rüdesheimer ..	$9\frac{1}{3}$	$8\frac{2}{3}$	$\frac{1}{3}$

The greatest difference is, therefore,  $\frac{2}{3}$ , and the least  $\frac{1}{4}$  per cent. I am more particularly disposed to prefer this method to any other, since inaccuracies will always occur, and it is always a question on which side they are committed. I consider myself justified in this preference, by the fact that in the five comparative experiments, the difference with regard to the distilled spirit is now positive and now negative. The spirit distilled from Bordeaux gave a less alcoholic content, and so did that distilled from Rüdesheimer; but in Port wine, Teneriffe, and Madeira, the alcoholic contents were greater. The kind of wine does not explain this difference; it depends upon the experiment, and its cause is still unknown. On this account a method which depends entirely upon evaporation is to be preferred, since it is sufficiently accurate, and more easily applicable.

In conclusion, I may remind the reader, that as a general rule, Port, and other heavily loaded wines,



ought not to be evaporated too far, as in that case a portion of the substances held in solution in wine are precipitated, and the result obtained is consequently less accurate. In expelling the alcohol it is of use to conduct the steam of hot water through the wine.

The volatile matters (alcohol and water excepted) which appear in wine, are too insignificant in quantity to affect the results. In determining the alcoholic contents of the wine from the distilled spirit they must be met with. Mayer,\* using Malaga wine, obtained very different results as to the alcoholic contents according as the wine was distilled, or the amount of alcohol calculated from the residue left after the wine had been evaporated and restored by means of water to its original volume. He found from 14 to 19 per cent. extract, and it becomes a question whether wines of the same kind as Malaga can be tested by this method.

The experiment was tried in the following manner: A solution of sugar was made, with which alcohol was mixed; a liquid was thus obtained, having, at 48·2 F. 9 C. to 50 F. 10 C. a specific gravity of 1·0407. Of this 200 CC. were taken.

Spirit was distilled from this liquid in a closed distilling apparatus, and water then added to the distilled spirit, and to that remaining in the retort, till both again=200 CC.

\* Journ. f. Pract. Pharm. Bd. 15, s. 201.

At the same temperature, the specific gravity of the solution of sugar = 1.0602, and that of the spirit, 0.9797. This last would give  $16\frac{2}{3}$  per cent. as the alcoholic contents, at 95.5 F. 15.5 C., whilst  $1.0407 - 0.0602 = 0.9805$ , gives an alcoholic per centage of 16. There is, according to this, a difference of  $\frac{2}{3}$  per cent. I consider, for such determinations, that this is sufficiently accurate.

It must be remembered that errors also will occur in distilling spirit, since all wines contain acetic acid; and therefore, if we would have distilled spirit alone, the wine must not be distilled by itself, but the process must be carried on after the addition of chalk.

Inaccuracies will always occur in such determinations, but for all technical purposes I consider the method of evaporation sufficiently accurate; though I must confess that neither this means nor the distillation of spirit can give the exact amount.

Blaanderen has obtained the following results from the wines mentioned. The determinations were all made between 48.2 F. 9 C. and 50 F. 10° C.

## Madeira—twelve kinds.

Specific gravity of the wine.		Sp. gr. of wine without alcohol.	Alcoholic contents per vol. 10°5 C.=50·9 F.	
No. 1	0·9971	1·0184	18	Average 19·1
2	0·9933	1·0169	20	
3	0·9947	1·0179	20	
4	0·9974	1·0192	18	
5	0·9930	1·0170	20	
6	0·9946	1·0179	20	
7	0·9972	1·0190	18	
8	0·9931	1·0176	21	
9	0·9953	1·0170	18	
10	0·9957	1·0172	18	
11	0·9946	1·0179	20	
12	0·9972	1·0190	18	

## Teneriffe—twelve kinds.

Specific gravity of the wine.		Sp. gr. of wine. without alcohol.	Alcoholic contents per vol. 10°5 C.=50·9 F.	
No. 1	0·9945	1·0154	17	Average 18·8
2	0·9933	1·0152	18	
3	0·9926	1·0152	19	
4	0·9909	1·0134	19	
5	0·9936	1·0160	19	
6	0·9925	1·0152	19	
7	0·9908	1·0131	19	
8	0·9930	1·0159	19	
9	0·9927	1·0164	20	
10	0·9985	1·0122	20	
11	0·9911	1·0122	17½	
12	0·9924	1·0151	19	

## Rhine wine\*—eleven kinds.

Specific gravity of the wine.		Sp. gr. of wine without alcohol.	Alcoholic contents per vol. 15° 5 C.=50° 9 F.	
No. 1	0·9960	1·0090	9½	Average 10·6
2	0·9951	1·0091	10	
3	0·9940	1·0083	11	
4	0·9935	1·0085	11½	
5	0·9948	1·0093	11	
6	0·9939	1·0085	11	
7	0·9934	1·0083	11	
8	0·9953	1·0095	11	
9	0·9957	1·0097	10	
10	0·9946	1·0086	10½	
11	0·9940	1·0084	11	

## Port wine—eleven kinds.

Specific gravity of the wine.		Sp. gr. of wine without alcohol.	Alcoholic contents per vol. 50° 9 F. 15° 5 C.	
No. 1	0·9970	1·0205	20	Average 19·3
2	0·9974	1·0192	18	
3	0·9966	1·0189	19	
4	0·9926	1·0167	21	
5	0·9971	1·0194	19	
6	0·9954	1·0188	20	
7	0·9932	1·0168	20	
8	0·9984	1·0207	19	
9	0·9999	1·0227	19	
10	0·9961	1·0188	19	
11	0·9970	1·0192	19	

\* I have not put down the names of the Rhine wines, as I could not give them accurately, but remark here, that all through this Treatise, when Madeira, Teneriffe, Rhin, or Port wine are mentioned, the same numbers are used to distinguish them as are given here.

The following wines have been examined in the same manner at a temperature of from 9 to 10 C. (48·2 to 50 F.) by Vlaanderen.

	Sp. gr. of the wine.	Sp. gr. of the wine without alcohol.	Alcohol per vol. 15·5 C. 50·9 F.	
Bordeaux . . . . .	0·9941	1·0086	10·5	red
Bordeaux Sauterre . . . . .	0·9937	1·0090	12	pale yellow
Bourgogne Beaune . . . . .	0·9939	1·0083	11	red
Hermitage . . . . .	0·9950	1·0095	11	red
Lachryma Christi . . . . .	1·0600	1·0805	17	brown
Muscot Rivesaltes . . . . .	1·0800	1·0946	11	yellowish white
Champagne Mousseux . . . . .	1·0200	1·0349	11	yellowish white
Benicarlo . . . . .	0·9947	1·0142	16	dark red
Roussillon . . . . .	0·9972	1·0143	13·5	dark red
St. George . . . . .	0·9950	1·0088	10	red
Narbonne . . . . .	0·9954	1·0115	12·5	dark red
Tavella . . . . .	0·9949	1·0094	11	light red
Langlade . . . . .	0·9926	1·0075	11	pale red
Côtes (white). . . . .	0·9922	1·0076	12	white
Bergerac (white) . . . . .	1·0958	1·1030	13·5	yellowish white
Bourgogne Pommard (old)	0·9945	1·0087	11	red

We may deduce from the above determinations, so far as they concern the relation between the specific gravity and alcoholic contents of wine, that the former cannot be taken as the standard of the latter. The reason of this is to be found in the great variety of substances held in solution in the wine. But even in the same kind of wine the specific gravity does not furnish the means for determining the alcoholic contents.

In comparing, for example, the different kinds of Port wine, we perceive a difference of from 0·9932 to 0·9999, whilst the former contains 20, the latter 19 per cent. alcohol. And the specific gravity of all kinds

containing 19 per cent. alcohol is found to be, 0·9999, —0·9984,—0·9971,—0·9970,—0·9966,—0·9961.

The same holds good in respect to other wines.

The quantity of alcohol, for example, in the Rhine wines, varies only between  $9\frac{1}{2}$  and  $11\frac{1}{2}$  per cent., whilst their densities range from 0·9934 to 0·9960. But among such Rhine wines as give 11 per cent. alcohol, we find the specific gravity 0·9953—0·9948 —0·9940—0·9939—0·9934. It cannot be otherwise.

The specific gravity of wine does not depend entirely upon the alcoholic contents, but is more or less affected by the non-volatile constituents.

I subjoin various analyses of the alcoholic contents of wine, with which other determinations are occasionally given these we shall understand better by-and-by, but in order to avoid repetition, I was obliged to put them together here.

Some of these numbers are inaccurate, more particularly because they have been obtained by means of an inaccurate method. In order to make my summary as complete as possible, I have selected such as are most generally known.

FONTENELLE. (French Wines.)

East Pyrenees.

	Vol. per cent.
Rivesaltes . . . . .	10·8
Banyules . . . . .	10·9
Collioure . . . . .	10·7
Salces . . . . .	10·1

## Département de l'Aude.

	Vol. per cent.
Fitou et Leucate . . . . .	10.1
Lapalme . . . . .	10.4
Sigean . . . . .	10.2
Narbonne . . . . .	9.9
Lezignan . . . . .	9.6
Merepeiset . . . . .	10.1
Carcassonne . . . . .	8.5

## Département de l'Herault.

Nissan . . . . .	9.3
Beziers . . . . .	9.1
Montagnac . . . . .	9.6
Mèze . . . . .	9.1
Montpellier . . . . .	8.7
Lunel . . . . .	8.9
Frontignan . . . . .	8.4
Hermitage (white) . . . . .	8.3
Bourgogne . . . . .	7.3
Graves . . . . .	6.9
Champagne non mousseux . . . . .	6.9
Champagne mousseux (white) . . . . .	6.1
Champagne mousseux (red) . . . . .	5.8
Bordeaux (best) . . . . .	7.3
Toulouse . . . . .	5.9

These determinations are all too low.

Payen gives the following numbers :\*—

	Vol. per cent.
Porto et Madera . . . . .	20
Bagnouls, Xéres, Lacryma Christi . . . . .	17
Grenache (old Madeira) . . . . .	16
Juraçon (white) . . . . .	15.2
„ (red) . . . . .	13.7
Vin de Lunel . . . . .	13.7
St. George, Malaga, Cyprus . . . . .	15

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\* Chimie industrielle.

	Vol. per cent.
Vauvert . . . . .	13·3
Frontignan . . . . .	11·8
Hermitage (white) . . . . .	15·5
Côte-Rotie . . . . .	11·3
Sauterne (white) . . . . .	15
Beaune (white) . . . . .	12·2
Barsac, 1. . . . .	14·7
"    2. . . . .	12·6
"    3. . . . .	12·1
Poudenzak, 1. . . . .	13·7
"    2. . . . .	13
"    3. . . . .	12·1
Claret (Bordeaux exported to London) . . . . .	13
Blaye . . . . .	10·25
Libourne . . . . .	9·85
Saint-Emillion . . . . .	9·18
Parsac . . . . .	9·45
La Réole . . . . .	8·50
Cubzac . . . . .	8·75
Château-Lafitte et Château-Margaux . . . . .	8·7
Château-Latour . . . . .	9·3
Giscours et Léoville . . . . .	9·1
Laroze-Kirwan . . . . .	9·8
Cantenac . . . . .	9·2
Tronquoy-Lalande . . . . .	9·9
Saint-Estèphe . . . . .	9·7
Volnay . . . . .	11
Mâcon . . . . .	10
Champagne mousseux . . . . .	10 à 11·6
Cher . . . . .	8·7
Coteaux-d'Angers . . . . .	12·9
Saumur . . . . .	9·9
Tokayer . . . . .	9·1
Rhine wine . . . . .	11 à 11·9
Chatillon . . . . .	7·5
Verrières . . . . .	6·2



Gay-Lussac\* (Payen's statements are omitted here):—

	Vol. per cent.
Château-Haut-Brion . . . . .	9
Château-Destournel . . . . .	9
Brannes-Mouton . . . . .	9
Lalagune . . . . .	9·3
Therme-Cantenac . . . . .	9·1
Phelan . . . . .	9·2
Good Burgundy . . . . .	11
Angers (coteaux) . . . . .	12
Vins de poids (from the South) . . . . .	13
Common Wine . . . . .	9·8
White Wine (from la Vendée) . . . . .	8·8
Wachenheim (Rhine) . . . . .	11·9
Forst . . . . .	11·5
Sherviles (lower Rhine) . . . . .	11
Westhoffen . . . . .	10
Bomme, white . . . . .	12·2
Saint-Pièrre-du-Mont . . . . .	11·5
Molsheim . . . . .	9·2
Bosheim . . . . .	8·6
Barr . . . . .	6·9
Ergersheim . . . . .	6

According to Malland,† French wines have the following alcoholic contents:—

	per cent.
Bourgogne (red) . . . . .	7·7
Macon (red) . . . . .	7·7
„ (white) . . . . .	7·1
Blois (red) . . . . .	7·3
Vouvray (white) . . . . .	9·7
Entre deux mers (white) . . . . .	9·0
Cher (red) . . . . .	8·0
St. Macaire (Gironde) (red) . . . . .	8·3
Joue (red) . . . . .	8·0
Anjou (white) . . . . .	10·0

\* Pélouze et Fremy, tom. iii. p. 436.

† Journ. de Chim. Méd. Juin 1842, p. 326.

	Per cent.
Piccardan (white) . . . . .	10·0
Blaye (white) . . . . .	8·3
Gaillac (Tarn et Garonne), red . . . . .	10·7
Chinon (red) . . . . .	8·3
Orleans (red) . . . . .	7·8
Sanserre (red) . . . . .	8·3
Selogne (white) . . . . .	8·7
Saint-Christol (red) . . . . .	11·0
De la Côte Chalonnaise, (red) . . . . .	9·0
St. Aignau (red) . . . . .	6·7
Tonnerre (red) . . . . .	7·3
Bergerac (white) . . . . .	13·7
Tavella . . . . .	14·0
Chablis . . . . .	7·5
Ponilly . . . . .	9·0

Most of these numbers are too low.

Fauré\* has analysed the wine of La Gironde, and the following tables are extracted from his statements.

WHITE WINE.

	Sp. Gr.	Alcohol per ct.	Solution of Gelatine required.	Enan- thin.
Castillon . . . . .	0·995	11	6·0	—
St. Foy . . . . .	0·996	11	4·8	—
Fronsac . . . . .	0·997	10·8	4·8	—
Sauterne . . . . .	0·995	15	4·0	1·1
Barsac 1. . . . .	0·995	14·8	4·3	1·1
„ 2. . . . .	0·995	12·7	4·5	0·9
„ 3. . . . .	0·994	12·3	4·7	0·6
Carbonnieux . . . . .	0·994	13·2	6·0	0·9
Poudensac 1. . . . .	0·997	13·8	4·3	0·9
„ 2. . . . .	0·997	13·1	4·4	0·7
„ 3. . . . .	0·997	12·3	4·8	0·5
Preignac . . . . .	0·996	11·5	6·0	0·5
Langoiran . . . . .	0·998	10·3	4·3	0·3

\* Journ. de Pharm. tom. vii. p. 200.

## RED WINE.

1840	Sp. Gr.	Alcohol per ct.	Solution of Gelatine required.	Ænan- thin.	Solution of Chlorine required.
Château Lafitte .....	0·996	8·7	10·1	1·2	12·3
„ margaux ....	0·996	9·8	9·3	1·3	11·4
„ Latour .....	0·995	9·3	13·3	1·1	15·3
„ Haut-Brion ..	0·994	9·0	7·0	1·1	11·3
Cos destournel .....	0·997	9·0	9·0	1·2	15·4
Brannes mouton .....	0·997	9·0	10·3	1·0	14·8
Léoville .....	0·996	9·2	8·0	1·1	13·5
Gr. la Rose .....	0·997	9·9	8·2	0·9	13·5
Kirwan Cantenac ....	0·997	9·3	9·3	0·9	14·3
Giscours .....	0·997	9·1	12·3	0·8	16·3
Lalagune .....	0·996	9·3	12·0	0·8	14·3
Therme-Cantenac ....	0·998	9·2	10·0	0·8	13·0
Tronquoy-Lalande .. .	0·997	9·9	9·9	0·8	16·3
St. Estephe Phélan....	0·998	9·8	7·0	0·9	13·5

The solution of gelatine was so prepared that 100 grammes precipitated 1 gramme (15·49 grs.) tannic acid. The chlorine water was prepared in the usual manner.

Alcoholic contents of wine at 15° 5 C. 50·9 F. according to Brande.

	Alcohol.
Port wine maximum . . . . .	23·92
Port wine minimum . . . . .	19·82
Madeira maximum . . . . .	22·61
Madeira minimum . . . . .	17·91
Constantia . . . . .	18·29
Lacryma Christi . . . . .	18·24
Xeres (Sherry) maximum . . . . .	18·37
„ „ minimum . . . . .	17·00
Lisbon . . . . .	17·45
Madeira (red) . . . . .	17·04
Cape Madeira . . . . .	16·77
Cape Muskat . . . . .	17·00
Calcavella . . . . .	16·76
Hermitage, (white) . . . . .	16·14
Malaga . . . . .	15·98
Roussillon . . . . .	15·96
Syracuse . . . . .	14·15

	Alcohol.
Bordeaux (Claret) maximum . . . . .	15·11
„ minimum . . . . .	11·95
Tinto (red French) . . . . .	12·32
Burgundy maximum . . . . .	12·32
„ minimum . . . . .	11·00
Graves (Bordeaux) . . . . .	11·84
Champagne, (white) . . . . .	11·84
„ (red) . . . . .	10·64
Rhine wine maximum . . . . .	13·31
„ minimum . . . . .	8·00
Tokay . . . . .	10·46
Nice . . . . .	13·5
Schiras . . . . .	14·4
Côtes-Rotie (Bourgogne) . . . . .	11·4
Frontignac . . . . .	11·8
Marsala maximum . . . . .	15·9
„ minimum . . . . .	14·2
Malmsey . . . . .	15·2
Bucellas . . . . .	17·1

## Bouis \* wine from the East Pyrenees.

	Sp. gr.	Alcohol. vol.
Perpignan (Labanera) . . . . . 1837	0·993	15
Baho (Garrigue) . . . . . „	0·994	15·4
Boges „ . . . . . „	0·994	14·57
Trouillas „ . . . . . „	0·994	15
Tressère „ . . . . . „	0·994	14·8
Palla „ . . . . . „	0·994	13·6
Corbère „ . . . . . „	0·999	13·9
Pia (Hortolanes) . . . . . „	0·992	10·27
Tornilles (Crete) . . . . . „	0·994	14·23
Corneille de la Rivière (Crete) . . . . . „	0·994	14·93
Baixas „ . . . . . „	0·996	14·5
Calce „ . . . . . „	0·993	14·2
Espira de l'Aigly „ . . . . . „	1·006	14·2
Mauri „ . . . . . „	0·989	14·7
Saint Paul „ . . . . . „	0·993	13·7
Saint Martin „ . . . . . „	0·992	12·9
Millas (Plaine) . . . . . „	0·993	14·6
Salées „ . . . . . „	0·994	13
Riversaltes „ . . . . . „	0·998	14·6
Céret (Côte Saint Féréol) . . . . . „	0·991	15·2

\* Brandes Arch. Bd. 25. s. 222.

	Sp. gr.	Alcohol.
Aoles (Côte au sud) . . . . . 1837	0·989	15
Argelés (Saint Magdalaine) . . . . . „	1·002	13·7
Collioure (Saint Jullien) . . . . . 1838	0·999	16·1
Rangals sur mer . . . . . „	1·040	15·9
Ille (Garrique) . . . . . 1837	0·993	16·27
Rhodez „ . . . . . „	0·987	14·53
Vinca „ . . . . . „	0·988	14·27
Finesbrat „ . . . . . „	0·988	14·43
Prades „ . . . . . „	0·993	13·87
Villefranche „ . . . . . „	0·992	13·6
Olette „ . . . . . „	0·994	13·6
Sijean „ . . . . . „	0·993	12·6
Fitou „ . . . . . „	0·994	11·3
Narbonne „ . . . . . „	0·993	13

Christison has given us the following analyses of the alcoholic contents of wine.

	In volume.
Port wine, weak . . . . .	18
„ average of 7 kinds . . . . .	20
„ (strong) . . . . .	21
„ (weak) . . . . .	18
Sherry (weak) . . . . .	17
„ (average of 13 old wines) . . . . .	18
„ (strong) . . . . .	20
„ (average of 9 kinds, East Indian) . . . . .	18
Madre de Xeres . . . . .	21
Madeira (long in East Indies, strong) . . . . .	21
„ „ „ „ (weak) . . . . .	17
Teneriffe (long in Calcutta) . . . . .	17
Cercial . . . . .	18
Lisbon sec. . . . .	20
Amontillado . . . . .	16
Claret. 1811 . . . . .	10
Chateaux Latour. 1815 . . . . .	10
Rosau. 1825 . . . . .	10
Claret ordin. (best kind) . . . . .	11
Rivesaltes . . . . .	11
Malmsey . . . . .	16
Rüdesheimer (best) . . . . .	10
„ (ordinary) . . . . .	9
Hambacher (best) . . . . .	9

I have used round numbers here, and given the volume calculated from Christison's weights. In Liebig's Annales,\* from which I have taken these statements, the temperature is not given.

Filhol† has analysed the wine of the Upper Garonne, principally with the view of ascertaining the effect produced by the weather during the summer upon the wine of different years. I subjoin some of his statements:—

Wine from		Spec. grav.	Intensity of colour.	Alcohol, 15°.	Tartar.	Tartrate of alumina	Tartrate of iron.
Villandrie .....	1841	0·922	1·0	12·6	0·8	0·04	0·05
„ .....	1844	0·993	—	11·1	0·9	Spur	0·13
Villemur .....	„	0·991	1·0	12·3	0·8	0·03	0·07
Fronton .....	„	0·995	1·0	12·3	1·2	} Spur	
Lardène .....	„	0·993	0·9	8·8	1·0		
Cornebarien .....	„	0·994	—	10·0	0·9		
Leguevin .....	„	0·992	0·6	10·7	1·2		
Portet .....	„	0·995	0·7	1·5	1·2	0·03	„
Saint Gaudens ....	„	0·996	0·2	8·6	1·0	0·05	„
„ „ ....	1842	0·993	—	10·1	0·8	0·04	0·04
„ „ ....	„	9·990	—	8·7	1·5	0·04	0·03
„ „ ....	„	0·997	—	—	1·6		
Martres.. .....	1843	0·991	—	11·2	1·3		
Verfeil .....	1844	0·994	0·4	9·1	1·3	0·05	—
Grénade .....	„	0·993	0·7	10·3	1·1	—	—
Levignac .....	„	0·992	—	10·3	1·2	—	—
Avignonet .....	„	0·992	0·3	10·3	1·6	0·03	0·05
Revel .....	„	0·994	0·6	8·6	—	—	—
„ .....	„	0·995	—	8·4	—	—	—
Merville .....	„	0·998	—	—	2·4	0·04	0·04
„ .....	1841	0·996	—	—	2·1	0·04	0·05

Filhol has determined the extract of wine, and taken

\* Bd. 37, s. 125.

† Journ. de Ch. Méd. 4 série, tom. ii. p. 251.

as a standard the consistence of pills. He finds in every kind, from 19 to 25 per cent. of this extract evaporated to the consistence of pills. But what is this consistence? He has also analysed the ashes of wine, but I think it unnecessary to state more than I have done. He found sulphate of lime and potash, chloride of calcium, and phosphate of lime.

Ludersdorf.*	Sp. gr.	Alcohol in per. c. Richter.	Extract.	Ammon. to satu- ration per cent.
Medoc Bourgogne .....	0.9960	7.4	1.9	10.1
Haut Sauterne .....	0.9940	9.8	2.1	9.3
Haut Bommès .....	0.9940	9.5	1.8	9.3
Haut Cenous .....	0.9940	8.5	2.0	13.2
Niersteiner .....	0.9971	8.8	1.9	10.1
Forster Riesling .....	0.9911	10.0	1.8	9.2
Markobrunner .....	0.9910	9.4	2.1	10.1
Oppenheimer .....	0.9910	9.9	1.8	8.5
Celtinger .....	0.9938	7.3	1.8	10.9
Pisporter .....	0.9930	6.7	1.8	10.6
Brauneberger .....	0.9940	7.9	1.5	10.1
Steinberger .....	0.9960	6.7	1.9	9.5
Ungsberger .....	0.9970	6.8	1.9	8.6
Rödelseer .....	0.9944	8.5	1.9	11.8
Leistenwein .....	0.9994	7.2	1.9	10.9
Naumburger .....	0.9975	6.4	2.3	16.0
Grüneberger .....	0.9976	6.5	2.1	15.0
Tokayer.....	1.0201	12.1	10.6	10.6

## Geiger.†

	Sp. gr.	Alcohol.	Extract.
Steinberger .....	1.0025	10.9	9.9
Rüdesheimer.....	1.0025	12.7	5.4
Markobrunner .....	0.9985	11.6	5.1
Geisenheimer .....	0.9935	12.6	3.1
Liebfrauenmilch .....	0.9939	10.6	2.3
Dienheimer .....	0.9925	9.8	2.2

\* Journ. f. Pract. Chem. Bd. 24. s. 102.

† Magazin f. Pharm. Bd. 19. s. 266.

	Sp. gr.	Alcohol.	Extract.
Weinheimer .....	0·9925	11·7	2·2
Bingen (Scharlachberg) .....	—	12·1	—
Wiesbaden (Nersberg) .....	0·9950	10·8	2·8
Wiesloch .....	0·9945	9·8	2·2

## Fischern.\*

Wine from the Palatinate.		Alcohol.	Ex-tract.	Sugar.	Sugar in the grape juice.
Liebfrauenmilch .....	1841	9·9	4·1	0·1	21·7
„ .....	1842	9·3	2·7	1·0	19·4
„ .....	1843	9·4	2·3	1·5	19·1
Luginslander .....	1834	9·5	2·7	1·1	19·7
Zeller (Riesling) .....	1846	9·8	2·7	1·3	20·3
„ „ best .....	„	9·3	7·3	3·5	23·9
„ (Traminer) .....	„	10·5	2·6	1·6	21·3
„ (Rulander) .....	„	10·4	2·7	1·5	21·2
Neckar wine.					
Eberstädter .....	1842	6·3	1·9	0·6	13·7
„ .....	1845	5·6	2·1	0·2	12·5
„ (white) .....	1846	8·4	2·7	0·7	18·0
„ (red) .....	„	9·4	2·4	1·4	19·4
Saxon, red					
Wine from the Spaarberg .....	1842	9·4	3·0	0·8	20·0
Hungarian Wine.					
Adlersberger .....	1827	9·3	2·6	1·2	19·3
Ruster Ausbruch .....	1834	11·4	10·7	6·1	30·1

Fusenius† has given us the analyses of some kinds of Rhine wine, four months old.

	Sp. gr.	Alcohol.	Free acid.	Grape sugar.	Ext. Tot.
1. Hattenheimer .....	0·9959	10·7	0·6	3·6	4·2
2. Markobrunner .....	1·0012	11·1	0·5	4·5	5·2
3. Steinberger .....	1·0070	10·1	0·5	4·5	5·6
4. „ Choice .....	1·0323	10·2	0·4	8·6	10·6

\* Ann. der Ch. u. Pharm. Bd. 58. S. 705.

† Ann. der Ch. u. Pharm. Bd. 63. S. 384.



The acid is calculated as tartaric acid, the grape sugar as free from water.

From this summary we may infer that the saccharine contents of the grape juice were originally from:—

1. ....	24.5 per cent.
2. ....	26.3 „
3. ....	24.1 „
4. ....	28.5 „

Beek \* found the sp. gravity of:

Madeira, three kinds .....	0.9866
„ (Sercial) .....	0.9861
London particular .....	0.9886
Port wine, two kinds .....	0.9820
Sauterne .....	0.9951
Claret, two kinds .....	0.9949
American Wine .....	1.0070

Diez,† a short time since, undertook the analyses of many Rhine wines.

Names of wine.		Spec. gr.	Alcohol vol.	Potash re-quired to saturate.	Sugar.	Extract at 100° (212 F.)	Ashes.
Forst, Choice ..	1852	0.9964	11.2	0.51	0.65	2.5	0.20
„ .....	1848	0.9957	11.4	0.48	0.63	2.5	0.13
„ .....	1846	0.9955	11.5	0.48	0.57	2.4	0.15
„ .....	1844	0.9954	11.6	0.48	0.43	2.4	0.14
„ .....	1834	0.9953	11.9	0.39	0.30	2.1	0.13
Deidesheim ....	1853	0.9998	11.2	0.76	0.78	3.2	0.15
„ Riesling ..		0.9988	10.9	0.78	0.69	3.2	0.15
„ Traminer ..		0.9997	11.8	0.68	0.68	3.2	0.17
„ .....	1848	0.9973	12.0	0.57	0.53	2.0	0.13
„ .....	1846	0.9953	12.1	0.47	0.11	2.0	0.14

\* Edinb. New. Phil. Journ. 1835; April—July, p. 145.

+ Ann. der Ch. u. Pharm. Bd. 96. s. 304.

Name of wine.		Spec. gr.	Alcohol vol.	Potash re- quired to saturate.	Sugar.	Extract at 100°. (212 F.)	Ashes.
Markobrunner.							
Choice .....	1822	0·9963	12·2	0·40	0·24	2·4	0·19
Rüdesheim ....	1848	0·9963	11·4	0·52	0·43	2·5	0·18
„ .....	1846	0·9957	11·6	0·33	0·39	2·1	0·15
Geisenheim ....	1848	0·9967	11·4	0·47	0·50	2·7	0·18
„ .....	1842	0·9960	12·2	0·40	0·43	2·3	0·18
Gimmelding ....	1852	0·9920	11·2	0·55	0·64	2·3	0·21
„ .....	1849	0·9910	12·0	0·46	0·55	2·1	0·15
Ruppertsb .....	1848	0·9956	11·5	0·46	0·57	2·4	0·16
„ .....	1834	0·9950	11·6	0·40	0·25	2·3	0·11
Dürkheim .....	1852	0·9960	11·4	0·55	0·64	2·1	0·18
„ .....	1849	0·9956	12·0	0·53	0·58	2·1	0·17
Hattenheim ....	1834	0·9960	11·9	0·39	0·27	2·0	0·16
Musbach .....	1842	0·9967	10·5	0·50	0·53	2·2	0·12
Neustadt .....	1852	0·9986	9·5	0·46	0·64	1·9	0·12
Ahrbleich .....	„	0·9960	11·2	0·39	0·67	2·9	0·23
Oppenheim ....	1848	0·9951	11·3	0·36	0·50	2·1	0·13
Ungstein .....	1853	0·9988	11·2	0·77	0·69	2·6	0·16
Wachenheim ....	1852	0·9963	11·4	0·57	0·63	1·9	0·17
Laubenheim ....	1846	0·9974	11·1	0·55	0·43	1·9	0·17
Rauenthal .....	1834	0·9962	12·1	0·48	0·28	2·1	0·20
Steinberger .....	1846	0·9955	11·6	0·41	0·35	2·1	0·15
Hochheim .....	„	0·9963	11·5	0·38	0·44	1·6	0·18
Pisporter .....	1848	0·9977	10·8	0·58	0·52	2·2	0·20
Scharlachberg....	„	0·9972	10·2	0·59	0·43	2·3	0·17
Nierstein .....	1842	0·9952	11·3	0·49	0·41	1·9	0·13
Bockenheim ....	1835	0·9961	11·0	0·56	0·33	2·4	0·18
Edenkoben .....	1850	0·9923	10·2	0·55	0·49	2·1	0·16
Johannesberg ....	1842	0·9917	10·0	0·51	0·42	2·1	0·12
Assmannshauser	1848	0·9957	11·2	0·44	0·34	2·5	0·23
Oberingelheimer	1846	0·9983	11·6	0·47	0·46	2·5	0·28

Zierl \* has determined the wines of Bavaria and the Palatinate halymetrically, and therefore, inaccurately.

			Sp. Gr.	Alcohol.	Extract.
Forster . . .	of	1834	0.9936	9.90	3.7
„ . . .	„	„	0.9868	10.77	2.3
„ . . .	„	„	0.9940	10.07	2.6
„ . . .	„	1822	0.9949	8.18	3.2
Deidesheimer .	„	1834	0.9951	10.35	2.5
„ . . .	„	„	0.9942	9.97	3.0
„ . . .	„	„	0.9944	9.56	2.0
„ . . .	„	1831	0.9959	7.92	2.8
Ruppertsberger	„	1834	0.9940	9.26	2.6
„ . . .	„	„	0.9935	10.07	3.1
Wachenheimer	„	„	0.9944	10.07	2.9
Durckheimer .	„	„	0.9949	9.33	2.4
Ungsteiner .	„	„	0.9944	9.02	2.7
Kahlstädter .	„	„	0.9961	9.91	3.1
Bockenheimer	„	„	0.9936	10.21	2.0
Freinsheimer	„	1811	1.0034	8.70	2.8

### Soubeiran. †

	Per. c. alcohol.
Johannesberger . . . . .	15 to 16
Rhine wine (good quality) . . . . .	11 „ 12
„ (less good) . . . . .	7 „ 10
Bagnoles . . . . .	17 „ 18
Coullioure . . . . .	15 „ 16

Schubert ‡ has analysed many of the Wurzburg wines.

		Sp. gr.	Alcohol.	Free acid calculated as tartaric acid.	Extract.
Riesling	1847	0.9938	8.6	0.82	2.8
„	1846	1.0083	9.1	0.56	7.2
Mixed .	„	0.9879	9.9	0.82	2.6
„ .	1845	0.9947	8.4	0.65	3.1

\* Baierisch. Kunst. u. Gewerbebl. 1838. s. 466.

† Traité de Pharm. 1847. tom. i. p. 129.

‡ Pogg. Ann. 1849. Bd. 77. s. 397.

		Sp. gr.	Alcohol.	Free acid reckoned as tartaric acid.	Extract.
Riesling	1844	0.9954	8.0	1.14	3.8
Mixed .	1842	0.9925	8.7	0.82	3.1
Traminer	1835	0.9762	7.2	0.90	3.6
Riesling	1834	0.9910	8.6	0.82	3.9
Mixed	1822	0.9954	9.6	0.91	4.2
"	1818	0.9937	8.8	1.06	2.8
"	1811	0.9946	8.9	0.91	3.2
"	1775	0.9925	10.4	0.91	4.4
"	1748	0.9950	9.1	1.06	3.3
"	"	0.9912	10.2	1.06	3.9
"	1847	0.9937	8.2	1.14	3.2
Riesling	1846	0.9907	9.9	0.65	3.1
Mixed	"	0.9900	10.5	0.65	2.9
"	1845	0.9925	7.8	0.82	2.7
"	1844	0.9925	8.4	0.82	2.6
Riesling	1842	0.9927	9.2	0.65	2.9
Mixed	1841	0.9925	8.7	0.90	2.8
"	1822	0.9910	9.2	1.35	3.5
"	1818	0.9933	9.3	0.85	3.1
"	1811	0.9929	8.0	0.91	3.3
"	1783	0.9946	8.1	1.02	3.5
"	1766	0.9921	10.7	0.69	3.9
"	1728	0.9971	8.3	1.14	3.3
"	1847	0.9933	8.3	0.91	2.8
Glävner	1847	0.9950	8.4	0.91	4.2
Traminer	1843	0.9954	8.4	0.91	2.9
Mixed	1822	0.9916	9.2	0.81	3.3
"	1783	0.9933	10.4	1.25	4.0
"	1845	0.9991	8.1	0.45	1.1
"	1847	0.9958	7.3	0.91	3.6
"	"	0.9958	7.9	0.91	3.6
Riesling	1846	0.9912	10.1	0.73	2.7
Mixed	"	0.9912	7.6	0.73	3.8
Traminer	1847	0.9916	8.4	0.91	3.1
Mixed	"	0.9926	6.4	1.06	2.6
"	1841	0.9980	9.8	0.82	2.7
Riesling	1847	0.9950	8.8	1.00	2.6
"	1846	0.9900	9.9	0.82	2.7

		Sp. gr.	Alcohol.	Free acid reckoned as tartaric acid.	Extract.
Traminer	1846	0.9883	10.0	0.65	3.5
Mixed	1822	0.9921	9.7	0.82	4.2
"	1818	0.9921	8.4	0.90	3.0
"	1847	0.9981	6.2	1.14	2.7
"	1842	0.9891	9.6	0.65	2.8

He has furnished us with other determinations of the wine, but those given are sufficient.

Kersting has given us an analysis of seven kinds of wine from the Bergstrasse.\*

Sp. gr.	Alcohol.	Sugar.	Free tartaric acid.	Extract and salts, without sugar and tartaric acid.
0.9936	8.2	0.3	0.8	1.3
0.9933	10.4	0.5	0.7	1.3
0.9934	9.0	0.2	0.7	1.2
0.9930	8.8	0.2	0.7	0.8
0.9916	10.0	0.2	0.6	0.9
0.9918	10.6	0.2	0.7	1.2
0.9924	10.7	0.2	0.6	1.6

Geromont† has analysed the alcoholic contents of wines from the neighbourhood of Bingen. They are arranged according to their Bouquet; but the temperature is not given, nor are we told whether weight or volume are intended.

Scharlachberger . . . . .	12.1
Gisler . . . . .	11.9
Kempterberg . . . . .	10.0
Mehlwag . . . . .	10.4

\* Ann. der Ch. u. Pharm. Bd. 70. s. 250.

† Liebig's Ann. Bd. 17. s. 158.

Mainzerweg . . . . .	10·7
” . . . . .	10·6
” . . . . .	8·3
Hundestrahel . . . . .	12·1
Delberg . . . . .	9·6
Dietersheimer (Landwein) . . . . .	6·1

Mitis\* has analysed the following wines, among others, and given us the alcohol in weight:—

	Alcohol.	Extract.
Wine from Greece . . . . .	10	4·8
Brunnerwein . . . . .1811	9	2·9
” . . . . .1822	10	2·6
Weidlinger . . . . .1834	10	3·3
Neustedler Wine . . . . .”	8	4·4
Grinzinger . . . . .1822	10	2·5
Maurer . . . . .1834	10	2·6
Kahlenberger . . . . .”	10	2·6
Gritzendorfer . . . . .”	10	2·6
Bisamberger . . . . .”	11	2·7
Gumpoldskirchner . . . . .1822	10	3·7
Haslacher Frankenwein . . . . .	8	3·0
Esfchendorfer . . . . .1822	9	3·0
Heinrichsleutner . . . . .”	10	4·2
Mosler . . . . .	9	2·5
Chateau-Margaux . . . . .	10	2·6
St. Estephe . . . . .	10	3·2
Good Champagne . . . . .	11	11·1
Effervescing Champagne . . . . .	9	12·6
Sicilian (Marsalla) . . . . .	17	4·5

Hitschok† has obtained the following results from an analysis of the wines of eastern countries:—

		Sp. gr.	Ext.	Alcohol.
Wine from Hebron . . . . .	1	1·0083	3·1	18
	2	1·0086	3·0	17

\* Baiersch. Kunst. u. Gewerbebl. 1838. C. 703.

† Edinb. New. Phil. Journ. 1834. Bd. 37, p. 176.

			Sp. gr.	Ext. Alcohol.
Wine from Libanon . . . .	1		1·0121	3·1 14
„ „ „ 1 year . . . .	2		—	— 14
„ „ „ 6 years . . . .	1		1·0892	9·6 10
	2		1·0880	9·6 11
„ from Syria . . . .	1		1·0051	2·4 14
	2		—	— 15
„ from Cyprus . . . .	1		1·0220	4·3 17
	2		1·0254	4·6 17
„ from Rhodes . . . .	1		0·9920	1·5 18
	2		0·9909	1·4 18
„ from Corfu . . . .	1		0·9930	1·4 16
	2		—	— 15
„ from Samos . . . .	1		1·0205	3·9 14
	2		1·0226	4·1 15
„ from Smyrna . . . .	2		1·0162	3·3 13
	2		—	— 13

Malaga wine has been analysed in detail by Mayer.

In seven kinds of this wine, prepared by boiling down the must, the following contents were found:—

Sp. gr.	Vol. of al. p. c.	Sugar.	Weight of extract per cent.
1·037	12·5	9·9	14·4
1·069	13·2	„	„
1·069	13·5	„	„
1·057	14·9	„	„
1·057	15·0	14·7	18·4
1·056	15·3	14·5	18·7
1·070	16·1	„	„

If we select one of the last two kinds given here, and calculate the sugar originally contained in the liquid from which this wine was prepared, we shall find it 40 per cent., the evaporation to which the grape juice was exposed having raised it to this amount.

Mayer obtained, as a precipitate by ammonia, 1·147—1·129—1·139 per cent. phosphate of ammonia and magnesia, and also sulphuric acid, lime, and tannic acid, and 0·38 per cent. ashes. The great quantity of phosphate of magnesia which may be precipitated from wine by means of ammonia, as double salt, is a proof of the genuineness of Malaga wine, since from no other wine is it obtained in like abundance, though of course, all wines which have been exposed to evaporation must yield more than such as have not been subjected to this process.

If we confine ourselves for the moment to the alcoholic contents of the most excellent wines, we shall find that even thus we are able to determine them, although the results obtained by the different analyses may at first sight seem to vary.

Port is one of the wines which is richest in alcohol. Ginjal has stated that genuine Port wines never contain more than 12·75 per cent. pure alcohol, and is of opinion that those who discovered more in such wines either analysed a wine which had been adulterated with alcohol, or were unable to determine accurately the strength of the alcohol.

It is difficult to pronounce upon this opinion of Ginjal's out of Portugal. But we may be permitted to ask one question. How is it that all who have analysed Port wine have found from 17 to 21 per cent. alcohol? Is there no wine except such as is adulterated with alcohol exported from Portugal? And



does Port wine, which is recognised as the strongest wine in the country which produces it, really belong to those not very strong wines which only contain 13 per cent. alcohol?

For my part I hesitate to accept Ginjal's statement, although his experiments were made in Portugal.

With regard to the alcoholic contents, Madeira ranks next to Port wine, in which respect they differ but little from each other. Liqueur wines are, as a rule, stronger than red wines; Jurançon, Lachryma Christi, Benicarlo, and Sauterne, all contain from 12 to 15 per cent. alcohol, and more. Red French wines contain less—from 9 to 14 per cent. Good Bordeaux contains 10, 11, 12 per cent.; Burgundy, 9, 10, 11 per cent.; Champagne, 10, 11 per cent. Rhine wine from 6 to 12 per cent., generally from 9 to 10 per cent.

## CHAPTER IX.

### TANNIC ACID IN WINE.

It has already been observed that not a trace of tannic acid is to be detected even in the juice of the purple grape, that this acid is principally found in coloured wines, and its amount is in proportion to the depth of the colour, so that light-coloured liqueur wines contain very little. This fact may be easily ascertained by adding a clear solution of isinglass to the wine; in the coloured wines it forms a strong precipitate, in the others is usually a scarcely perceptible one. The addition of salt of oxide of iron makes the precipitate more evident, thus a trace of tannic acid can be always detected in old and colourless wines.

I know nothing about the existence of gallic acid in wine, though it is so easily produced from tannic acid. Its absence need not, however, surprise us, since free admission of air is necessary to the conversion of tannic into gallic acid, and such admission is not allowed in wine. If the tannic acid of red and other wine be precipitated by means of isinglass, and filtered, the addition of salt of oxide of iron does not produce a dark colour, a proof that gallic acid does not exist.

Nevertheless, I am of opinion that a trace of gallic acid may easily occur in wine.

We have seen that no tannic acid exists in the grape juice. If it is found in liqueur, or colourless wine, it proceeds either from the skins which were allowed to ferment, or from such sparingly soluble substances as passed into the juice during the pressing and crushing of the grape-skins. It may also proceed partially from the fruit-stalls, or from the grape-stones, if these have been allowed to ferment, since they contain a good deal of tannic acid.

The amount of tannic acid in Madeira, Rhine, Teneriffe, Muscadel, Champagne, and other wines which are not red, may be wholly disregarded when considering them medically, or dietetically, for the quantity is too insignificant to affect even their flavour; at least the wines we are now considering have not, as is well known, a trace of astringency in their flavour. It is, however, a question, whether such wines as contain but little sugar do not owe their flavour, at least partially, to tannic acid.

I have not attempted to determine the tannic acid contents of wine, because I was not acquainted with any method of accomplishing it in such a manner as to be largely and generally useful.

I can safely assert that traces of tannic acid may be found in all white wines. A scarcely perceptible trace was detected by means of chloride of iron in Bordeaux Sauterne; it was more perceptible in Cham-

pagne, still more so in Madeira, Teneriffe, and Rhine wines, and proportionably strong in Muscadel and Lachryma Christi.

Fauré has determined the amount of tannic acid in the white wines of la Gironde by means of isinglass, and found from 4 to 6 parts in 10,000 parts of wine (p. 172). This appears to me to be too much, and I must also doubt whether so insignificant an amount of tannic acid could be accurately determined by a standard solution of gelatine.

The same may be said with respect to the determining the amount of tannic acid in red wines. Judging from the colour produced by chloride of iron and the precipitate formed by isinglass in red wine, I should expect in general to find four or six times as much tannic acid as in liqueur wines (which mostly contain it), but Fauré as mean gives only twice as much; indeed in 10,000 parts wine he found six parts tannic acid in white Castillon, and only seven parts in red Haut Brion.

The difference between red Burgundy and red Bordeaux in respect to the tannic acid they contain, is very perceptible, the former always containing less than the latter.

Dark-coloured wines deserve especial notice with regard to the tannic acid they contain. Port wine is among the darkest, though many French wines come near it in point of colour. As far as is known, young Port wine contains the greatest quantity of tannic

acid, and holds the largest amount of colouring matter in solution. The wine is not red, but dark violet, and contains in proportion but a small quantity of free acid.

Young Port wine, when drawn off into bottles, and clear, deposits without intermission, and during a series of years, a sediment of organic matters which may be loosed from the lower parts of the bottle in complete cakes.

The more copious the deposit, the clearer will be the colour of the wine. The violet hue which it had when young becomes red, then yellowish red, and at length yellow; at last the colour agrees so exactly with that of liqueur wine as to make it often difficult to distinguish Port wine by the colour alone from Madeira, and other wines. The alterations which Port wine undergoes are such as are common in a greater or less degree to all other heavily loaded wines, and in all such a deposit is formed, and the colour of the wine rendered lighter, becoming dark yellow instead of red. This colour is well known in strong old cellared Bordeaux wines. If these wines are left in casks which are kept properly filed, the alteration takes place more quickly than in bottles.

A great deal of tannic acid is contained in Port and heavily loaded Bordeaux wines. The oxygen of the air which is either dissolved in wine, or present in the bottles or casks, oxidises this tannic acid to a substance which is sparingly soluble, and is called by Berzelius apothema, or precipitate of tannic acid.

This substance, whilst becoming insoluble, unites with the colouring matter, just as albumen and gelatine, which, when put into wine, coagulate, and by precipitating the colouring matter, discolour the wine.

But although albumen or gelatine, if copiously added to young Port wine, almost deprive it of colour, this result is not possible if the colouring matter be precipitated with the apothema of tannic acid. Apothema is not quite insoluble in weak spirit, as, for example, in wine; enough remains in the wine to colour it yellow. Whilst Port wine is forming a deposit, diminution takes place both in the tannic acid and dissolved colouring matter contained in it. The deposit is apothema of tannic acid, which is intimately combined with the colouring matter of the wine. As much apothema remains in solution in old Port wine as is found in Madeira, and such liqueur wines, and the colour of the Port wine becomes the same as that of these liqueur wines.

This explanation entirely agrees with all the reactions which might here serve as illustrations. In the first place, if isinglass be carefully added to very young Port wine, tannic acid and colouring matter may indeed be precipitated, but no yellow colouring matter remains in solution, such as is possessed by old Port wine; and further, in Port wine which has been long cellared, a yellow colour is distinctly perceptible after a precipitate of tannic acid and colouring matter has been obtained by the judicious application of isinglass,

and the older the Port wine the more apparent is the yellow colouring. This is a plain proof that the yellow colouring matter did not originally exist, but is afterwards formed in the wine.

I obtained results like the above from analysing the cake-like deposits of Port wine. They were taken from very old Port wine, and had undergone all the alterations which were possible to them under the circumstances.

It was first necessary to examine whether the yellow colour of the old Port was attributable to these substances; that is, whether a small portion of them was still held in solution in the wine. In order to ascertain this, the above-mentioned deposit was extracted with warm alcohol, it was sufficiently soluble to impart to the liquid a colour which, when cool, exactly agreed with that of Port wine. The liquid, filtered from some of the insoluble constituents, was deprived of colour by means of basic acetate of lead, and all the yellow substance combined with oxide of lead. This lead precipitate was, after being washed, suspended in water, and decomposed by means of sulphuretted hydrogen; the water passed through clear, whilst the sulphide of lead, treated with boiling water, imparted to it a yellow colour.

The watery solution, when exposed to evaporation, deposited a dark-coloured substance, soluble in water. No precipitate was obtained from this solution when

mixed with solution of gelatine till after an acid had been added, and then the whole of the brown substance was contained in the precipitate.

Exactly the same substance may be obtained from Port wine itself. Port wine was precipitated with acetate of lead, the precipitate washed, suspended in water, and sulphuretted hydrogen conducted through it, and the liquid afterwards filtered. After the sulphide of lead had been boiled with water, and the solution evaporated, the addition of solution of gelatine was not sufficient to produce a precipitate, but it was necessary to add acid. The result obtained was, that the yellow colouring matter of the Port wine agreed exactly with a portion of the sediment deposited in the course of time.

These properties agree entirely with those which Berzelius has published as peculiar to apothema of tannic acid. Pélouze found that a diluted solution of tannic acid becomes brownish yellow when exposed to the air; and any one who chooses to expose solution of tannic acid to the air, may, after a time, perceive the alteration in the colour, which appears darker or lighter according as the solution is more or less concentrated. This change is not, however, to be considered exactly the same as that which tannic acid undergoes when exposed to heat; for, at the usual temperature, not only is colour changed, but gallic acid formed, and the discoloration may be viewed as partial decomposition of the sugar of tannic acid



into ulmic acid, or some similar substance. Up to this time gallic acid has not been sought in that solution of tannic acid which has been rendered deep brown, by being heated during exposure to the air, otherwise it might perhaps have been discovered. Here, also, it can only be the sugar of the tannic acid which gives rise to a humus-like substance, which, in this case, combines with a portion of the tannic acid, and is thereby precipitated. What therefore is called apothema of tannic acid, is a humus-like substance combined with tannic acid. Berzelius has given the following method of analysis: Let the dissolved tannic acid which has become brown by the action of heat be precipitated with sugar of lead, washed with water, the precipitate dissolved in water and decomposed by means of sulphuretted hydrogen. The tannic acid remains in solution in the water, and in the sulphide of lead a dark-coloured substance is deposited, which is best removed by the use of ammonia, when it yields a dark-coloured solution, and after evaporation deposits a blackish brown substance almost tasteless, and soluble in water. This solution cannot be precipitated by means of solution of gelatine, unless an acid be added, which gives rise to a brown gelatinous precipitate. I retain the term apothema, although the substance is really of the nature of humus. From all that has been said, the following inferences may be deduced:—

*a.* That the yellow colour of old Port wine is the

effect of apothema of tannic acid, small quantities of which are soluble in weak spirit.

*b.* That excepting a trace of yellow-coloured substance, no peculiar yellow substance is to be found in Port wine, nothing, that is, which could proceed from the grape skins.

*c.* That therefore no peculiar yellow colouring matter need be sought for in red wine which has been cellared, since tannic acid is found in all wines, which necessarily becomes apothema, and this apothema must colour the old wine.

*d.* That in this manner the old French wines becoming yellow is sufficiently explained.

*e.* That the liqueur wines, which originally contain but little tannic acid, and cannot therefore form a precipitate, nevertheless become yellow in the course of time, and this change in their colour may, perhaps, be accounted for in the same way, namely, by the formation of a small quantity of apothema of tannic acid.

*f.* That only such wines as are produced from dark purple grapes (which contain a great deal of tannic acid), the skins of which were allowed to ferment, and which therefore contain tannic acid in excess, can form cakes of sediment, when the fermentation is completed.

*g.* That this cake-like sediment is apothema of tannic acid, the excess of which could not be dissolved in the wine; and this was formed from the tannic acid by the oxygen of the air.

We shall be able to speak still more clearly, and in detail, about this matter, when we have considered the colouring matter of wine.

The preservation of the wine is in a great measure to be ascribed to tannic acid, for the albuminous matters, which are always combined with tannic acid in wine, are thus prevented from decomposition, and the principal cause of the wine spoiling is thereby checked. Wines therefore which are intended for exportation, or to be long cellared, must not be deprived of too much tannic acid by means of albumen or gelatine (p. 98).

It has been observed that if red wine be put into well-corked glass bottles, and exposed to full daylight, a flocculent precipitate is obtained, and the colouring matter in this manner withdrawn from the wine. The flavour and aroma of the wine do not suffer. The first phenomenon is easily explained. Light promotes the production of apothema from tannic, especially if sufficient air be admitted. The apothema thus produced is insoluble, and withdraws the colouring matter from the wine by virtue of the so-called surface attraction.

It would be impossible for light to act in this matter unless a sufficiency of air were dissolved in the wine, but a large quantity is unnecessary, and some air is always present in all wine.

## CHAPTER X.

### COLOURING MATTERS IN WINE.

ALTHOUGH there are almost innumerable shades of difference in the colour of wine, they are all varieties of two, the reddish and the yellowish colour. I say *reddish*, for we know no kind of wine that is actually red or yellow. What we call red in wine is violet, a mixture of blue and red. We do not in chemistry speak of the reddish wine as red, but designate its hue by the term wine-colour; it is the colour which is imparted to litmus by means of boracic acid and carbonic acid, and which, according to Malaguti, can only be made to change into the red colour produced by the action of hydrochloric acid on litmus, by the addition of large quantities of these acids.

What we call yellow wine is not yellow, but pale brown. For who has ever seen yellow wine? Madeira, and such like wines, are brown, but for the sake of convenience we shall continue to call them yellow.

Besides these, there are wines which every one calls brown: those, namely, which have been boiled, such as Tinto, and the like. We will now direct our attention to the cause of this variety of colour.

As we find among so-called yellow wines a variety which extends from such as are almost colourless to the dark brown, we must endeavour to explain this whole series of varieties—and as red wines vary from more or less crimson to the darkest purple red, and yet become yellow in the course of time, it may not be superfluous to dwell a little upon these points.

Endless variety may result from one and the same cause. Supposing the amount of blue colouring matter reddening by means of acids to exist in equal quantities in all red wines, a variation in the quantity of cream of tartar, or of an acid salt, will still cause a difference in the colour. The addition of a single milligramme (.015 gr.) of cream of tartar in a bottle of wine makes it redder, or *vice versa*, darker. But besides cream of tartar, free tartaric acid is found in many, and malic acid in some wines. In proportion to the amount of free tartaric and malic acid will be the redness of the wine. The same holds good with respect to acetic acid which is found in all wines.

But the quantity of colouring matter is also variable; and in proportion to its excess, an equal amount of acids being assumed, the colour of the wine will be darker, since a fixed quantity of acid is necessary to make the colouring matter of wine red.

In order to understand this subject clearly, it will be advisable in treating of it to begin with the facts derived from experience, and hence, first, that all red wines, without distinction, owe their colour to one and

the same blue colouring matter; and second, that no peculiar colouring matter is found in liqueur wines.

We shall endeavour to treat these two points rather in detail, since what has already been scientifically stated with respect to them is either inaccurate or incomplete.

In considering the preparation of wine, care must be taken to keep in mind the difference occasioned by the fermenting or non-fermenting of the skins, stalks, and stones.

Wine produced from grape juice alone is colourless, or white. The fact that the whole mass of grapes is pressed together renders it impossible but that a slight admixture of the components of the grape skins should occur, and in this manner a portion of the tannic acid contained in the skins is dissolved, and passes into the wine.

We have seen that white wine may be prepared from purple grapes. But if the skins were allowed to ferment, red or yellow wine would be obtained, according as purple or white grapes were used.

Liqueur wines are obtained from white grapes, the skins of which were permitted to ferment with the juice.

Perfectly colourless wines are never met with; a tinge of yellow may be found even in such as have least positive colour. Among such as are nearly as clear as water, the Italian wine, *vino cebedino*, may be especially mentioned.

It is obvious that the cause of the slight yellow colour which may be discerned in such wines, is not to be found in any particular substance which deserves the name of colouring matter, for vegetable juices, well or ill preserved, or heated, when in contact with the air, never appear perfectly colourless. Those substances which impart a brown tinge to colourless vegetable juices when allowed to evaporate, and with which the chemist is still but little acquainted, can, when brought into contact with the air, suffer a like alteration at a common temperature.

We may therefore expect to find in colourless wines, when they have been prepared from grape juice alone, without any admixture of skins, a more or less perceptible yellow colouring—the result of the slow oxidation of a substance known by Scheele as soapy-matter, to which Vauquelin first gave the name of extractive matter, since it constitutes the principal part of medicinal extracts—a substance spread over the whole vegetable kingdom, and capable of assuming, as De Saussure observed, a brown colour, by absorbing oxygen, and giving off carbonic acid, when exposed to the action of air and heat.

This substance is found not only in the juices of the leaves and fruits, but in every part of vegetable products. It becomes gradually browner and browner, but in a diluted state is called yellow. It is this substance which is present in grape juice, and when brought into contact with the air becomes more and

more deeply coloured. Here, then, we discover one reason for the pale brown colour common to wines which are not red. It is not necessary that the grape juice should ferment in order that this extractive matter may oxidize and acquire a brown tint; on the contrary, its oxidation appears to be rather checked than promoted by fermentation, as we learn from the white grapes which have dried in the sun.

Is any one acquainted with white raisins?

The extractive matter being oxidized, and from colourless having become brown, a substance is formed which, though then soluble in water and spirit, is rendered insoluble by continued exposure to the air, and resolved into a substance which is called by Berzelius deposit (absatz) or apothema.

This body is of a humus-like nature, possessing other qualities in common with humic acid, besides that of dissolving with a brown colour in alkali, or carbonated alkali, from which it may again be precipitated by means of acids. It is sparingly soluble in alcohol.

The substance described above being always contained in fermented grape juice, necessarily renders it darker in the course of time, especially if free access be allowed to the air, and this is the case when wine is preserved in casks, and frequently drawn off into others, as at every transfer it is saturated with air.

If the wine be evaporated by heat before fer-



mentation, apothema will form in it very quickly, and the colour of the wine becomes actually brown. Boiled wines (so called on account of the evaporation they undergo), such as Malaga, Tinto, &c., without possessing any peculiar colouring matter, are thus rendered brown, and their colour will be dark in proportion to the heat to which they were exposed, or the length of time during which they were in contact with the air. Evaporated grape juice leaves as residue a dark brown substance. But even wine that is almost colourless yields, when allowed to evaporate in the air upon a water bath, a dark brown extract, the colour of which must be attributed to the above-mentioned causes.

Every so-called apothema is a humic acid, and frequently bears traces of the substance from which it originates; hence the slight differences in their qualities. We talk, therefore, of the apothema of extractive matter, apothema of tannic acid, &c. What kind of humic acid it may be is not yet determined, perhaps it is apocrenic acid.

Wines prepared from white grapes, in which the skins have been allowed to ferment, are much yellower, sometimes, indeed, dark yellow; these are known as liqueur wines. Whilst the juice of these grapes ferments, the wine, which is in process of formation, extracts tannic acid from the skins of the white grapes, and holds it in solution.

Such a wine must in course of time acquire more

and more colour. Every solution of tannic acid, particularly when combined with other organic substances, acquires colour when exposed to the air. It is therefore eventually resolved into a sediment, apothema, a brown matter, which possesses some properties in common with the above-mentioned apothema, of extractive matter. If the solution contain but little tannic acid, the colour called yellow may become dark yellow, or actually brown, if much, much darker. The dark colour of mahogany is derived from the apothema produced from the tannic acid contained in the wood. Precisely the same observations may be made with respect to our wild chestnuts, which are covered with a perfectly white skin, so long as the seed is protected by the husk, but when this bursts, become dark brown in the space of a few hours. Without maintaining that the yellow colour of Muscadel, Champagne, and even of Teneriffe and Madeira, is to be entirely ascribed to the alteration thus undergone by tannic acid, it is true that the yellow hue is in great part to be attributed to this and the extractive matter before mentioned. For in these yellow or dark-coloured wines, the darker the colour originally was, the more intense is the colour given on the addition of a salt of iron. This reaction holds so true in general with respect to all liqueur wines, that the less the colour produced in any wine by the addition of chloride of iron, the lighter its colour originally was.

Pure Rhine wine is generally considered to be ex-

cellent in proportion as it is yellow, and a perfect agreement is found to subsist between the colour of the wine and that which it assumes, in consequence of its larger contents of tannic acid, when salt of oxide of iron is added to it. Now, as the tannic acid, the sugar of which has been converted into humic acid, is derived from the grape skins, and not from the juice, we can readily understand that tannic acid, as a colouring matter, may be employed in regulating the colour of liqueur wines, according as many or few grape skins are allowed to ferment in the juice. The colour depends upon the same cause which determines that of Cognac, pure French brandy, exported in oaken casks, whereby a little tannic acid passes from the wood into the wine, and is converted into apothema by the oxygen of the air. This example of Cognac, which is decisive, since it is coloured by nothing else, teaches us that oxidized tannic acid is the principal cause of the dark yellow or even brown yellow colour of wines. We learn that the same cause makes these wines in bottle gradually become darker. Atmospheric air is dissolved in bottled wine, since alcohol absorbs far more air than water, and hence it is that when alcohol is mixed with water a great deal of atmospheric air is expelled. In a mixture of alcohol and water, consequently in wine, more air will be dissolved than in water alone. The oxygen of this air and that which is contained in the upper parts of bottles not quite full of wine, is sufficient to oxidize so much of

the tannic acid of wine to apothema as shall insure the wine's becoming darker, for, indeed, only a very small quantity of oxygen is necessary to effect this. The effect is produced very slowly, and so the wine only seems to darken year by year. The insignificant quantity of tannic acid contained originally in the wine decreases in the same proportion, and at last disappears entirely.

In some wines the alteration in colour is very speedily effected. Trommsdorff\* gives us instances of white Bordeaux and Rhine wines, whose colour when exposed to the air quickly became so dark as to rival that of Malaga. The French wines in which he perceived this occur were Haut, Brassac, and Haut Sauterne, but he once saw the same thing in Liebfrankenmilch, the colour of which in a very short time nearly equalled that of old Jurançon. He thought he should find more tannic acid in the wine, but of course he did not, for if the colour was really produced from apothema of tannic acid, precisely the same amount of tannic acid must have disappeared.

We are not quite in the dark as to the causes of this phenomenon. The wines which Trommsdorff mentions had been protected from the air, and when again exposed to it very quickly became dark. We cannot doubt that in this case tannic acid was resolved into apothema. But the question is, why this change was not effected until the wine was exposed to the

\* Neues Journal der Pharm. Bd. 24, St. 2, S. 119.

air. It is quite certain that these wines had, during their preparation, been very little in contact with air, had been very soon bottled, and had not been frequently drawn. If at an earlier period they had been sufficiently exposed to the air, they would gradually have acquired more intensity of colour, and not have altered at once on coming in contact with air. Fauré has observed the fact commented upon (p. 118), that so much tannic acid as is necessary to turn wine black when exposed to the air, may be extracted by the wine from the wood of the casks.

We have seen, in speaking of Port wine (p. 190), that the oxidizing action of air on the tannic acid of wine is stronger in proportion as the amount of tannic acid exceeds what is commonly met with in liqueur wines. In these latter the resolution of colourless tannic acid into brown apothema is checked by the sugar. In wine poor in sugar and rich in tannic acid this is quickly changed into apothema, the wine becoming deep yellow. In wines which are rich in sugar and poor in alcohol, the production of apothema is slow, since the sugar hinders its formation.

Now, if we confine our attention to the variety of colour which may be produced in pure colourless wine, by means of a small portion of a brown substance, we must allow that such variety in the colour may be fully explained, first, by a difference in its solubility in a weaker or stronger alcoholic liquid; secondly, by a difference in its solubility in a liquid con-

taining more or less sugar; and lastly, by a difference in the quantity of apothema existing in such wines. Those wines which eventually become darkest, had originally most tannic acid and extractive matter, and as a rule were rich in sugar and gum. This apothema dissolves as well in water as in alcohol, and if sugar does not promote its solution, it does its mixing with the liquid in the form of particles which cannot be looked upon as dissolved; and gum, in particular, produces this effect. The grape juice from which Teneriffe, Madeira, Muscadel, and such like wines are produced, is colourless, just as Cognac is when put into casks; no peculiar colouring matter is contained in it, and the causes mentioned concur in producing in it, after a time, a colour resembling that of Madeira and other wines of the same sort.

Several phenomena indicate apothema of tannic acid as the principal source of the yellow colour of white wines. In the first place, if they are prepared from white grapes, the shorter the time during which the juice and the skins are allowed to be in contact whilst undergoing pressing (the tannic acid is contained in the skins, not in the juice), the more colourless will be the wine. And besides this, the wine does not remain white, unless the new oak casks (which contain tannic acid) have been carefully washed, for the tannic acid contained in the cask passes into the wine and is dissolved (p. 118). But since it is impossible to prepare white wine, in

which no trace of tannic acid shall be found, as some little is always absorbed, either from the skins or the wood of the casks, the wine-grower's experience teaches him that the wine will remain white in proportion as it is excluded, from the very first, from the air, which is necessary to the formation of apothema of tannic acid. All this agrees exactly with what we said of the cause of the yellow colour of liqueur wine.

I have, I believe, represented the cause of the colour of wines which are not red, in the simplest possible form, and freed it from the obscurity which encompassed it, so long as we were taught that every shade of colour, in white or liqueur wines, was to be accounted for by a peculiar colouring matter. In truth, there are at most only two colouring matters, both apothemata, one of tannic acid, and one of the soapy matter.

Madeira and Teneriffe wine were precipitated with sugar of lead, and filtered. A faintly coloured yellow liquid, which could not be attributed to the apothema of tannic acid, was obtained. Its intensity did not amount to one-tenth of the colour of Madeira or Teneriffe. This yellow tinge can be ascribed only to those mixed organic substances which render wine extract so dark after evaporation. One of its constituents is apothema of extractive matter.

The precipitate of sugar of lead, which is brown, contains principally the colouring matters of Madeira and Teneriffe. If it be suspended in water, and sul-

phuretted hydrogen conducted through it, a brown substance may be extracted from the sulphide of lead, by means of alcohol and tartaric acid. A tincture of the original colour of the wine is thus obtained, and the sulphide of lead contains nothing more.

If this tincture be evaporated upon a water-bath, and the residue treated with water, the whole is not dissolved (a), but a portion remains undissolved, which, however, is easily soluble in diluted ammonia, to which it imparts a brown colour. Both are, therefore, apothema, but both want the reaction of the apothema of tannic acid; for by gelatine and sulphuric acid, no precipitate can be obtained from it. However, the progress of decomposition entirely destroys all tannic acid reaction in apothema of tannic acid. When it is first formed a precipitate may be obtained by the addition of gelatine and acid; but after further decomposition it loses this reaction, and the apothema of tannic acid becomes exactly like apothema which has been produced in a different manner.

The brown substance (a), which is soluble in ammonia, but not in water, was re-precipitated by means of sulphuric acid. The above-mentioned experiments sufficiently prove that no peculiar colouring matter is contained in the above-mentioned liqueur wines, which are both distinguished by equal intensity of colour. In considering the extractive matter of wine we shall enter upon certain details which belong to this subject; at present we will only observe, that



the pale yellow colour of the liquid which flowed from the precipitate with sugar of lead, may be precipitated by means of basic acetate of lead; that if this precipitate be suspended in water, and sulphuretted hydrogen passed through it, a brown substance will be dissolved out from the sulphide of lead, by means of alcohol and tartaric acid, which comports itself in precisely the same manner as that which was deposited in the sulphide of lead previously mentioned.

The two precipitates of sulphide of lead, when they were afterwards extracted by means of ammonia, yielded nothing more. The apothemata are soluble in alcohol, and such acids as tartaric acid.

We may remark, as the conclusion of the whole investigation, that no peculiar colouring matter is to be detected in the two liqueur wines mentioned above; their colours must be ascribed to apothemata, which have been produced from tannic acid and extractive matter, by the action of the air; that apothema of tannic acid has here lost its distinctive character by the continued action of oxygen, and no longer yields a precipitate when mixed with acid and gelatine.

From white and liqueur wines, I turn to red or reddish, which, whether very dark or bright coloured, differ entirely from such as are called yellow.

There appear to be some few kinds of grapes which under a purple skin conceal a red juice. I have never seen them, but have found it stated that wine is prepared from such grapes without any closer descrip-

tion or analysis of them. This wine must, therefore, be red, even if it be prepared without the skins being permitted to ferment.

What we call red wine, is wine prepared from either black, purple, or red grapes, the juice of which is colourless, and the skins of which are allowed to ferment. During fermentation the weak spirit which is formed extracts not only tannic acid, but blue colouring matter from the skins. This blue colouring matter is tinged more or less red by the tartaric acid of the wine, and may afterwards be rendered more decidedly red by the formation of acetic acid. In the change of colour undergone by red wine five periods must be distinguished. As soon as alcoholic liquid is formed during fermentation, blue colouring matter begins to be extracted from the skins. As the small amount of blue colouring matter is brought into contact with grape juice, which has an acid reaction, it becomes red. The fermentation and formation of alcohol proceed, as does also the solution of the blue colouring matter; hence there is seldom sufficient tartaric acid to redden the blue colouring matter, and the young wine is rather blue than red, and may be called dark violet. This, new wine now undergoes after fermentation (p. 91), during which a great deal of colouring matter and red tartar, as well as albumen and apothema of tannic acid, is precipitated. The loss of the colouring matter causes the wine to become lighter. In the meantime the formation of acetic acid

begins, and at a later period increases; the amount of colouring matter is not thereby diminished, but the larger proportion of acid in the liquid reddens its colour. Another period now begins, during which the tannic acid is slowly converted into apothema, whereby red colouring matter is again precipitated out of the liquid, for example in Port wine; it thus gradually diminishes, and finally, after a length of time, disappears entirely from the wine, which then remains what is called yellow.

The fact that difference of time causes perceptible variety in the colour of red wines of the same kind, is thus explained by the various circumstances in which the colouring matter finds itself.

We are only acquainted with one kind of colouring matter, and there is no reason for supposing that more than one kind exists, however great the variety of colour in wines may be. Let us now consider the variety of circumstances which may influence the colour produced by one colouring matter, before we proceed to describe the colouring matter itself.

If a particular wine obtains by fermentation only 10 per cent. alcohol, whilst another rises to 16 per cent., then supposing a sufficient quantity of blue colouring matter present in the skins, the latter, as young wine, will be much darker coloured than the former, since colouring matter dissolves far more readily in alcohol and tartaric acid, than in water and tartaric acid. This explains why

purple grapes, which are rich in albumen and sugar, impart a darker colour to the wine. As a rule, young dark-coloured wines are stronger than others. The darker they are the more tannic acid was originally contained in them; and these are the wines which become yellow in course of time, and lose almost all their tannic acid by the formation of apothema, which withdraws the colouring matter from the liquid. This is the case with Port wine, whilst in many French wines relatively more colouring matter than tannic acid is contained, in consequence of which, though they give rise to apothema, yet they never become yellow without retaining a considerable tinge of bluish red colour.

The colour must also necessarily be affected by the amount of acid, be it free tartaric, or acetic contained in the wine. The wine will be redder the more free acid it contains; the brighter it is the less yellow, and the less apothema is formed and exists in solution. A perceptible difference in colour is likewise occasioned by a small difference in the amount of cream of tartar contained in the wine. But the difference of colour does not depend entirely upon these causes. The amount of colouring matter and of tannic acid differs even in purple grape skins; some are so dark as to be nearly black, others again are light purple, and of course light and dark wines will be respectively produced.

Lastly, the skins may be left for a longer or shorter

time in the liquid (p. 92), all, or a portion of the skins may be allowed to ferment, and white and purple grapes may be mixed, pressed, and allowed to ferment together. In the first case a darker, in the two latter a lighter wine will be obtained, the colour of which will, when the wine has been some time cellared, preserve the medium between red and liqueur wines. So that, although only one colouring matter is to be detected, variety of colour, almost without limit, may be found in red wine.

As when examining white and liqueur wines we found that their variety of colour was to be ascribed to a humus-like body formed in them, so in red wine the like variety may be explained by the single colouring matter which, with the apothema, explains all; and we may therefore contemplate this subject, which presents so many different aspects, from a single point of view. Here I must premise a question—Who has seen every existing variety of wine? or, who is qualified to pass an opinion upon all the different kinds of grapes? Therefore, in ascribing the red colour of red wines to two substances, one blue and one brown (apothema), and finding in this latter substance the origin of the colour of white and liqueur, I must be understood to speak of wines which I have seen and examined: such wines, that is, as are sold and used in our time and country.

I will now consider more particularly, and in detail, the actual colouring matter of red wine.

This colouring matter is not a product of fermentation, nor is it in any way altered by fermentation; it exists in the skins of purple grapes, and may be extracted from them with precisely the same qualities as from any kind of wine; as has been already mentioned (p. 42).

The manner in which I was most successful in preparing pure blue colouring matter from Bordeaux wine was as follows:—

The wine is precipitated by means of sugar of lead, and the dirty pale blue deposit collected upon a filter. As the liquid which passes through possesses an acid, reaction from acetic acid, it is pale violet. A little is lost by washing; but when the liquid employed for washing becomes neutral, what flows through becomes colourless. This precipitate is suspended in water through which sulphuretted hydrogen is then conducted. The sulphide of lead is filtered off, and the liquid, which then contains much tartaric acid, flows through tolerably red, and it is so when washed with water; but when the liquid becomes neutral it remains colourless.

Whether or no blue colouring matter be combined with oxide of lead may be doubtful; but it is certain that it is not chemically combined with sulphide of lead, it is held back by this in the same manner as by animal charcoal.

But this blue colouring matter is not entirely dissolved by boiling sulphide of lead with water. The

water is only slightly coloured yellow by a little apothema of tannic acid, which still remains in it; and in order to remove which, boiling with water is necessary.

After boiling, the colouring matter is found nearly pure in the sulphide of lead. Tartaric acid, gum, sugar, tannic acid, &c., and all inorganic salts, are all withdrawn, but not the fat.

Since colouring matter is insoluble in alcohol, it is not separated by boiling sulphide of lead with alcohol. It is completely insoluble in alcohol; may however be dissolved in alcohol with acetic acid, and still better in alcohol and tartaric acid, when it forms a beautiful red tincture. If the sulphide of lead be entirely freed from red colouring matter by alcohol and tartaric acid, no apothema of tannic acid can be removed from it by means of ammonia, since it has already been dissolved out from the sulphide of lead by the boiling water.

I will first endeavour to prove that no apothema of tannic acid exists with the red colouring matter in the alcoholic tartaric acid extract. If the tartaric acid in the red alcoholic tincture be carefully saturated with ammonia, tartrate of ammonia will be precipitated.

The liquid when nearly saturated with ammonia, and freed from tartrate of ammonia by the addition of alcohol, has the colour of a pale solution of chrome alum without a tinge of brown. It cannot be evapo-

rated without decomposition, and even at an ordinary temperature the colouring matter of wine cannot bear any excess of alkali, nor even of ammonia, without becoming speedily brown.

It cannot therefore be isolated in this manner.

There is only one method by which I have been able to obtain pure blue colouring matter of wine isolated. Sulphide of lead, freed from apothema by means of boiling water, is extracted with alcohol and strong acetic acid. The colouring matter is sufficiently soluble in it, though more sparingly so than in alcohol and tartaric acid. The alcoholic liquid containing acetic acid is then evaporated, when it first becomes red like wine; then, after evaporation, violet; and lastly, if a little acetic acid be present, of a singularly beautiful blue. Fat is at the same time separated. If the liquid be now evaporated to dryness, the fat extracted with ether, and a trace of the oxide of lead with acetic acid, the colouring matter remains perfectly pure.

The colour is bluish black, like black lead; I have never been able to obtain it in crystals. It is quite insoluble in alcohol, water, ether, chloroform, sulphide of carbon, olive and turpentine oil. Whatever has been maintained to the contrary, it is perfectly insoluble in all these liquids. I have already said that it is blue in the solution. Much blue colouring matter, when put into alcohol with a trace of acetic acid, yields a singularly beautiful pure blue liquid; more acetic acid makes it red. We may become acquainted with this



colouring matter when combined with an acid, by means of the solution in alcohol and tartaric acid. In a perfectly pure state it is perfectly soluble in alcohol and tartaric acid, though only in small quantities, and yet, after being dried, it required some hours to dissolve. It then yielded a singularly beautiful red tincture, and thus we may study its deportment in the circumstances in which it is found in wine. It is then red, not wine-coloured.

It is insoluble in ether combined with tartaric acid, as also in chloroform and sulphide of carbon. If therefore the solution in tartaric acid be agitated with one of these three liquids, they remain colourless.

If any dilute ammonia be added to the solution in alcohol and tartaric acid, it will, after complete saturation, become blue; if too little be added, it exhibits the above-mentioned colour of chrome alum.

The blue colour is likewise attainable by adding, with the greatest caution, potash, soda, or lime-water; and the addition of an acid will restore the colour.

As the blue precipitate is obtained by means of basic acetate of lead, and sugar of lead, we have here a chemical compound to deal with. The oxide of lead supplants the acid which made the blue colouring matter red. The colouring matter of wine, which is pure blue, forms a blue compound with oxide of lead.

And thus the colouring matter is a body capable of replacing a base or an acid; it displaces the acetic acid, which had combined with oxide of lead, unites with

this as a blue salt, and may be dissolved with a red colour in acetic acid and alcohol.

If a little more ammonia be added to the red solution of the colouring matter in alcohol and tartaric acid, the colour, which a moment before was blue, becomes green. If an acid be now added, the red colour is restored, but is not so bright as before. If the ammonia acts for a few moments, or if more be added, it becomes brown. The green colour was a mixture of blue and pale brown, which exhibits itself as yellow. And an alteration had therefore already occurred in the colouring matter. And if the continued operation of ammonia render it brown, the red colour cannot again be restored to it by means of acid. Hence ammonia decomposes the blue colouring matter.

This property, possessed in a still higher degree by potash, soda, and lime, if added in excess, indicates an alteration similar to that undergone by tannic acid, grape sugar, and many other bodies. Quercitrin, a yellow colouring matter, and many others, including quercetin, which is prepared from quercitrin, are easily changed by ammonia.\*

No satisfactory explanation of this fact can be given; we only know that the colouring matter of wine may be easily decomposed by alkalies, and must content ourselves with this knowledge.

At any rate we now understand why wines which

\* Rigaud in the *Ann. des Pharm.* Bd. 90, s. 283.

have become turned, are darker coloured, and why a copious addition of potash or lime, completely destroys the colour of wine (p. 125).

Though the colouring matter is thus easily affected by alkalies, it is proportionably insensible to strong acids. If oil of vitriol be dropped into its solution in alcohol, and tartaric acid, the colour becomes bright and strong red; excess renders the colour rather violet, but dilution with water restores the pure red.

Nitric acid when not too strong renders the colour brighter, but heat decomposes it.

If chlorine water be carefully dropped into the solution it loses its colour and becomes brown. In this new form it is to a certain extent constant, for even if no more chlorine water be added, the brown colour is retained, whilst in case of a further addition, the brown substance is discoloured, and becomes bright yellow.

This peculiarity is important, since Fauré deduces from it that two colouring matters exist in wine.

There may be two coloured substances contained in it,—red colouring matter and apothema of tannic acid (194). But in preparing the blue colouring matter, the apothema was removed, and the reaction, which Fauré ascribes to two colouring matters, proceeds from the pure colouring matter of wine.

Chlorine acts first upon the red colouring matter in the same manner as alkalies, which cause it to turn brown when exposed to the air. The first operation

of chlorine is likewise a first oxidation, and further oxidation of the newly-formed brown substance may be occasioned by the addition of more chlorine. The same holds good of tannic acid; chlorine and alkalies make it brown. Fauré's conclusion, drawn from this reaction, is however incorrect; he has viewed the two distinct operations of chlorine upon the pure colouring matter, as a proof of the presence of two bodies.

The alteration in colour undergone by the colouring matter of wine, under the operation of some salts, is very remarkable. I have taken the concentrated alcoholic tartaric acid solution, in order to see if it would fall with the precipitate, which is occasionally formed by some tartaric acid salts.

It remains dissolved in a solution of nitrate of silver, and becomes of a deeper red; sublimate makes it rather paler; subnitrate of mercury does not alter it at all; chloride of tin makes it darker red and slightly violet; nitrate of lead brighter red. With the exception of those obtained by sublimate the precipitates of tartaric acid salts are white; the colouring matter is not precipitated with them, but remains in the liquid under the influence of the stronger acids; alum produces no change in it.

It comports itself very differently with acetate of alumina, and with acetate and phosphate of soda, a little excess of acetic acid being present in all; these give it a violet hue very much resembling the colour

of wine ; in a dilute solution, like wine and water, the violet colour is a little deeper.

When acetate of alumina is employed, no precipitate is obtained from the liquid, which remains quite clear, but the bright red hue of the colouring matter of wine gives place to a violet shade.

This circumstance is of great importance in the theory of chemical affinities. It teaches us that the blue colouring matter of the wine is half combined with alumina and half with acid, that it is chemically and yet not entirely combined. We shall understand what is here meant better if we remember what was said p. 216, that sugar of lead in red wine yields a pale dirty blue precipitate. Apothema is found in it, and therefore it is no longer pure pale blue, and the quantity of tartrate of lead present in it renders it pale blue. Pure colouring matter combined with pure oxide of lead yields a pure blue precipitate. Hence, if the two ingredients be perfectly pure, the compound will be blue.

But a liquid containing acetic acid, and at the same time acetate of lead, is obtained from the precipitate of sugar of lead in red wine. Red colouring matter is more or less soluble in acetic acid and water. But when it flows from the precipitate, which acetate of lead yields in red wine, it is not red but violet, a mixture of red and blue.

It is this same colour which remains dissolved without becoming turbid in acetate of alumina.

We learn, therefore, that this mixed colour, as it exists in the liquid containing oxide of lead and acetic acid, and in that containing alumina and acetic acid, is neither free nor combined, but half-and-half; that it divides or contends with acetic acid for the combination with the base. Perhaps a double combination is formed of colouring matter, acetic acid and alumina, or of colouring matter, acetic acid and oxide of lead. The deportment of the half-blue, half-red colour of the colouring matter of wine in these combinations, is exactly like that of one equivalent of tartaric acid in cream of tartar, which retains its acid reaction.

I have dwelt upon these circumstances not so much on account of their intrinsic value, as for two other reasons. First, in order to recommend great caution in using reagents for the sake of detecting adulterations in red wine, since the least difference in genuine wine, or in the reagent employed, may perceptibly affect the colour; and secondly, to see if in this way we could obtain any more satisfactory explanation of the peculiar colour of red wine. It follows from what has been said, that the *blue* colouring matter in wine is chemically divided between tartaric or some other free acid, and a substance which acts as a base; just as it is divided between acetic acid and alumina in its violet colour in acetate of alumina. It does not dissolve in tartaric acid with water or alcohol with a pure wine colour, but red. If tannic acid be

added it remains red, and this is not, therefore, the cause of wine colour in wine. If a trace of gum or albumen be added the colour remains bright red. Hence some of the constituents of wine have no effect upon its colour. The colour must, therefore, be produced by some body possessing basic properties, and which can at least act instead of a base, since it is able to neutralise the strong tartaric and acetic acids of the wine. We must not forget that grape juice itself has an acid reaction, and contains free acids, and that in wine, acetic acid is added to tartaric acid. Sugar added to red solution of colouring matter has no effect upon the colour.

In short, I have never been able to obtain pure wine colour by adding one or many of the components of wine to a red solution of colouring matter; it was and remained red. The case is simpler here. If the solution of colouring matter in alcohol with tartaric acid be diluted with water, the genuine wine colour is produced. The addition of this water makes the colouring matter less soluble, and gives it a colour differing from what it has when more completely dissolved in pure alcohol and tartaric acid.

From 10 to 20 per cent. alcohol is contained in wine; I am speaking of red wines. The free acids or the cream of tartar cannot retain the colouring matter in complete solution, and even if the colouring matter be chemically divided among the ingredients of wine, as is the case with acetate of alumina, the fact that

colouring matter is but sparingly soluble in alcohol and water sufficiently explains the peculiar colour it has in wine.

For the same reasons strong acids, as sulphuric and nitric acids, by dissolving the colouring matter, more completely make it redder than tartaric acid.

I must here insert the following remarks. It is known that carbonic, boracic and other weak acids, impart to so-called blue vegetable colouring matters a wine colour, *e. g.* litmus tincture, not a bright red, as do muriatic and sulphuric acids. These weak acids stand in the same relation to the ammonia of the litmus colouring matter as do acetic acid and alumina to that of wine, that is, they take part in the combination, but neither is able completely to overpower the other.

Muriatic acid overpowers ammonia in litmus. Boracic acid does not. What remains of the blue colouring matter is insignificant in quantity, but may be easily distinguished; the effect of the ammonia is almost, though not entirely, removed.

The details respecting the colouring matter common to all red wine, which have thus been narrated, give us a large view of the endless variety in colour of which red wine is capable. The colour is not determined entirely by the quantity of colouring matter present, for it partly depends on the quantity of free acids, and is also affected by the quantity of substances which compete with acids, and are, like



them, capable of combining with colouring matter. Moreover, the colours of wines depend not only on the existing apothema of tannic acid, but more especially upon the greater or less solubility of the red colouring matter, therefore upon the greater or less alcoholic contents of the wine in combination with larger or smaller contents of free acids, or cream of tartar. I have confined myself to the properties of the colouring matter of wine as it appears when dissolved in tartaric acid and alcohol, in order to explain more particularly its relations with wine.

Colouring matter, when extracted from Burgundy, Bordeaux, and Port wine, exhibits precisely the same properties. The amount found in various kinds of wine varies greatly. A few bottles of ordinary Bordeaux furnish enough to allow its reaction to be studied, though if prepared in the manner indicated above, loss is sustained both when the liquid is filtered from the precipitate by sugar of lead, and when the sulphide of lead obtained from the precipitate of sugar of lead is washed with water; the loss being in this case occasioned by tartaric acid, which has become free.

I have convinced myself that no other red colouring matter can be found in these two liquids than what can be extracted from sulphide of lead by means of alcohol and acetic acid.

I must remark in concluding, that the colouring matter if prepared in this manner may easily have

a little sulphur and oxide of lead mixed with it. The first is dissolved with ether, which removes the fat; the latter with water, to which a little acetic acid has been added.

In Port wine, and other such wines as have been cellared and were originally dark, two colouring matters may be distinguished, one of which is the red colouring matter of red wine, and the other the apothema of tannic acid. In order to detect both and separate them, the following method must be adopted: Let Port wine be precipitated with sugar of lead, and a dirty deposit is obtained; if this be washed, a colourless liquid flows from it. If the precipitate, after being washed, be suspended in water and filtered, after sulphuretted hydrogen has been conducted through it, the liquid will be tinged with pale yellow.

The sulphide of lead, when well washed, is found to contain both red colouring matter and apothema. If it be treated with warm alcohol and tartaric acid, a tincture is obtained of the original colour of Port wine, which is redder if the wine be young, or browner if it be old. The colouring bodies are found mixed in it.

If this liquid, which contains both tartaric acid and alcohol, be digested with chalk, evaporated upon a water-bath and allowed to dry, then treated with water till the last traces of acid reaction disappear, boiled with water and filtered, the apothema is obtained as a brown liquid, while the red colouring mat-

ter, by means of alcohol and tartaric acid, can be extracted from the tartrate of lime, which remains undissolved.

The scaly precipitate from Port wine, extracted with warm alcohol and tartaric acid, gives a yellow tincture like very old Port wine. If this tincture be treated with chalk, boiling produces no brown solution, the apothema has become insoluble, as is the case with humic acid and humin; the latter is insoluble in water, and the former sparingly soluble. If the sulphide of lead (from the precipitate obtained from Port wine by means of sugar of lead) be treated with warm water, the apothema of tannic acid is dissolved out, and if the sulphide of lead be then extracted with alcohol and tartaric acid, the colouring matter of the wine is dissolved in it with a red, but not a Port wine colour. But if obtained from old Port wine, the amount is very insignificant: the younger the wine is the more red colouring matter it yields.

Doubts might justly be raised as to whether the alteration in colour undergone by Port wine and other heavily-loaded wine, is entirely the result of the oxidation of tannic acid and extractive matter, and of the precipitation of blue colouring matter, which is carried away with the apothema, which has become insoluble. Pure blue colouring matter may, however, be prepared from the precipitate in Port wine, which does not by precipitation suffer alteration.

That the colouring matter does not necessarily

undergo alteration may be proved in other ways. First, by the fact, that the removal of tannic acid by means of albumen, or isinglass, causes colouring matter to be deposited, as in younger wines; that is, that colouring matter which does not combine with either albumen or isinglass. But a still better example may be given. Henry has observed that the colour of red wine may be altered by quinine. Quinine combines with the tannic acid of the wine, and forms an insoluble salt, which precipitates the colouring matter with it.

It cannot be doubted that colouring matter and tannic acid are combined in the wine. Colouring matter combines with acids, and certainly with tannic acid also. It is undetermined how far this results from the chemical combination of quinine and tannic acid, and how far it is the consequence of the so-called surface attraction. But the experiment with quinine as explanatory of the change produced in the colour of Port wine, in consequence of the formation of apothema of tannic acid by which the colouring matter is withdrawn from the wine, is of sufficient importance to deserve our attention. Red wine needs only to have powdered quinine mixed with it, in order to become perceptibly discoloured, and to deposit a precipitate in which both blue colouring matter and tannate of quinine are found.

Two circumstances must, however, here be considered. Wine which has been much discoloured by

quinine is not pale red, but violet coloured. Quinine first combines with tartaric acid, in which latter ingredient the colouring matter is held in solution; tartrate of quinine, having lost the capability of retaining it, it is then of necessity precipitated. Secondly, the alkaline quinine, although so feebly alkaline, will have some action on the colouring matter of wine, which is so easily affected by alkalies.

There are, therefore, not one, but three causes for the action of quinine upon red wine.

Burgundy, when treated in the same manner as Bordeaux, that is, precipitated with sugar of lead, the precipitate decomposed with sulphuretted hydrogen, the sulphide of lead which is separated, washed, and extracted with alcohol and acetic acid, yields a tincture which differs neither in colour nor reaction from that which has been described in speaking of Bordeaux; that is, supposing the sulphide of lead to be previously freed from the apothema which clings to it; as it did likewise in Bordeaux.

The colour of Burgundy does not, therefore, depend entirely either upon a peculiar colouring matter, or the admixture of a foreign element, but principally upon smaller contents of free tartaric, or acetic acid.

We shall see that Burgundy contains exceedingly little acetic acid, less than any other wines which have been analysed. A darker and bluer colour is connected with this smaller amount of free acetic acid. And in fact this is proved in Burgundy. The

amount of free acetic acid varies so much in Burgundy, that though its darker colour cannot be entirely ascribed to the small amount of acetic acid, it must still be regarded as one of the principal causes.

It is well known that Burgundy is not affected in the same manner by time as other dark-coloured wines, Port, for example.

The insignificant amount of tannic acid contained in this wine is the reason; on account of this the wine spoils easily, and but little apothema (by which the colouring matter of wine is precipitated out of the solution) is formed by time in it.

This fact, and the less amount of oxygen contained in it, account for Burgundy wines being darker, and remaining so, if they can be preserved for a length of time.

I think the colouring matters of wine have been now sufficiently discussed, and it only remains for me to consider the best analyses, and compare them with the above.

We pass over liqueur-wines at once, since there are no analyses of them worth noticing.

Fauré's Analyses, given in his "Analyse chimique et comparée des Vins du Département de la Gironde," 1844, must first be mentioned. He speaks of two colouring matters in red wine; one blue, which dissolves easily in water, sparingly in alcohol, and is insoluble in ether; and one yellow, which is soluble

in all these liquids. A solution of the yellow colouring matter in ether being at first but slightly coloured, becomes after evaporation, if left to itself, and especially if exposed to the rays of the sun, first rose-coloured, then reddish, and at last violet.

In proportion as one or other of these colouring matters preponderates, the colour of the wine will vary. Fauré says that he was able to decompose the blue by chlorine without altering the yellow. When tannic acid preponderates over the colouring matter, the wines become discoloured by gelatine; when the contrary is the case they retain a rose-colour.

Fauré is mistaken respecting the solubility of blue colouring matter in water and alcohol. He probably employed water with the addition of an acid or salt, and it seems that he was not acquainted with colouring matter in a pure state.

The yellow colouring matter which Fauré detected in wine he considers to be a compound of two substances, which he confounds with one another. He first overlooks the apothema which is found in all red wines; and secondly, is of opinion that the blue colouring matter which, when slightly affected by chlorine becomes brown, is a constituent of wine: it is really the product of oxidation of blue colouring matter (p. 222), which if further decomposed by the addition of more chlorine, becomes pale yellow. This explains how Fauré came to imagine that blue colouring matter could be decomposed without the yellow

(brown) being thereby implicated. Everything, therefore, which Fauré has said about the colouring matters of wine is proved to be incorrect.

Batilliat, in his "Traité sur les Vins de la France,"\* also gives two colouring matters in red wine, rosit and purpurit. The first is rose-coloured, soluble in water and alcohol, but not in ether, and cannot be precipitated out of water by gelatine or albumen: it is principally found in the sediment of young wine. The second is blackish dark red, of astringent taste, soluble in water and ether, but not in alcohol; soluble in sulphuric acid, and may be precipitated out of it by water. Mixed with gelatine it gives a precipitate insoluble in alcohol and water, which may be found in the deposit of old wines. Fauré and Batilliat differ as to the solubility of the two substances in alcohol and water, or ether. Rosit gives a coal which is hardly combustible, and leaves a small amount of alkaline ashes. Batilliat never obtained it quite pure. It dissolves in concentrated sulphuric acid, and is precipitable with gelatine. It was obtained from the first sediment of wine when extracted with alcohol, filtered and evaporated, and the residue treated with water in which the rosit, and not the purpurit was found, dissolved. The watery solution is freed from tannic acid by gelatine, and evaporated.

No pure substance can, however, be obtained in this manner. Batilliat would have obtained nothing

\* P. 73, 1848.



had not the sediment contained a little free acid; probably he had a mixture of all such substances as, being in the sediment, are soluble in alcohol and water, except tannic acid, which he precipitated with gelatine.

According to Batilliat, nearly the whole of the sediment of old wine is composed of purpurit. After combustion, lime, iron, and potash are found in it. This purpurit exhibits itself so evidently as a mixture of blue colouring matter and apothema of tannic acid, that no further proofs are needed.

What, therefore, Batilliat has adduced respecting the colouring matter of wine is likewise inaccurate.

It would be by no means a useless undertaking to compare the colouring matter of wine with that of other plants or fruits. This is almost necessary to a thorough acquaintance with wine, especially if adulterations are to be detected. I should not have hesitated to make the attempt myself, had it been possible to obtain fruits for this purpose at that season of the year in which these analyses were made, but I must now defer it to another time. I consider it not improbable that the same blue colouring matter may be met with in other fruits.

Many colouring matters have the property of undergoing rapid transformation when exposed to the action of air. Berzelius\* notices the alteration undergone by the colouring matter of cherries and black-

\* Lehrbuch, Bd. 7, s. 159.

berries, and, as far as possible, he excludes the air when examining them. We have not found the colouring matter of wine variable, at least not when combined with acid. A watery extract of purple grape-skins became mouldy after being for a few days exposed to the air, but it still remained pure red. And in all the examinations we instituted a like result was obtained. The colouring matter cannot in the least bear a raised temperature or the action of alkalis.

I interpolate these remarks for the sake of explaining how colouring matter remains unchanged in all wines. It suffers no alteration; it does not originate the sediment which forms in red wine, since it combines and is deposited with another substance, which gradually becomes insoluble. It has the same properties in young and old wine.

These observations are of value when considering the manner in which the colour of some red French wines become gradually darker in the course of time. If the colouring matter of wine were gradually to change colour, it would be impossible to separate it pure, and this is nevertheless possible. Wines which become darker, owe the change in colour to the diminution of their acid contents, and the quantity of acetic acid which has been converted into acetic ether, and to the decomposition of tartaric acid or its compounds—alterations which we have already considered (p. 110).

Nothing more clearly proves the durability of the

colouring matter of wine when in contact with air, than the possibility of extracting it pure from old, red, crude tartar.

In concluding, I must just make an observation on a trace of tannate of iron salt which occurs in most wines, and when only present in a very small quantity, adds something to the colour of wine, but it can by no means give the wine the colour of ink, since tartaric acid decomposes tannate of iron, though less readily than oxalic acid; and free tartaric acid exists in wine.

## CHAPTER XI.

### IRON IN WINE.

FAURE detected minute quantities of tartrate of iron in French wines, but this iron salt is probably not found in it. Fauré found three parts tartrate of iron in 10,000 parts wine to be the maximum (p. 172). Let us now hear what Durozien, the reporter of Fauré's works, says in the *Journ. de Pharm.* 1844, tom. vi. p. 208; speaking of this homœopathic quantity of iron, we take more every day in meat, bread, vegetables, &c.

“M. Fauré qui le premier en a signalé l'existence, rappelle la vieille réputation des vins de Bordeaux comme propres à fortifier les enfans, à ranimer les convalescens, à soutenir les vieillards : cette réputation si bien acquise est demeurée sans rivale ce serait à la présence du sel ferrugineux qu'il faudrait la rapporter ; nous le reconnaissons volontiers avec notre confrère et nous nous félicitons avec lui de voir entrer dans la thérapeutique ce produit que la raison, le goût et la mode elle-même adopteront sans doute avec une égale faveur.”

It is a pity that the quantity of iron is too small to

justify this admirable sentence. But it is sufficient to colour red wine, which contains very little free tartaric acid so as to make it darker, and to give to white wines, which contain tannic acid, a darker tinge than tannic acid alone can produce.

In Burgundy, which contains but little free tartaric acid, the dark colour of the wine may, to a certain extent, be ascribed to the tannate of oxide of iron; for if a little tartaric acid be added to a diluted solution of chloride of iron and tannic acid, it retains the black colour. The wine being coloured by tannate of oxide of iron or not, depends, therefore, entirely on the quantity of free tartaric acid contained in it.

When red wine is mixed with a chalybeate water, we generally ascribe the dark colour it assumes to the ferruginous contents of the water; but Bischof\* has justly contradicted this erroneous view. The carbonate of potass of the water saturates the free acid of the wine, and so destroys the red colour; but the action of the alkali upon the colouring matter produces a dirty hue, which becomes the more unsightly in proportion to the preponderance of the alkali, and the length of time during which it acts upon the colouring matter (p. 218).

\* Tromsdorff N. Journ. Bd 13, st. 2, s. 321.

## CHAPTER XII.

### ON THE FATTY MATTER OF WINE.

IN describing the pure blue colouring matter of wine (p. 216), I mentioned a quantity of fat which adheres to the sulphide of lead, and must be removed from it by means of ether, as, otherwise, the colouring matter remains impure.

If the only point to be considered were the preparation of the fat, it would only be necessary to extract it with ether. This fat exists in wine as a fatty acid, for sugar of lead precipitates it out of the wine; the pale blue deposit exhibits itself as fatty, since the water used for washing does not wet it. There is, therefore, a fatty acid contained in the wine, which is resolved by sugar of lead into lead soap.

Batilliat\* separated fat from must, in the form of a fatty oil, and ascribed it to the grape stones. He considers the amount present too insignificant to affect the wine, but forgets that only  $\frac{1}{40000}$  of œnanthic ether is found in wine. The fat separated from the sulphide of lead by means of ether, was found by Oudemans to amount to 0·105 in 1875 grammes, that is, to 6 parts in 100,000 parts wine; not enough, certainly, for any one to grow fat upon.

\* *Traité sur les Vins de France*, p. 82.

## CHAPTER XIII.

### FREE ACIDS IN WINE.

FREE acids are found in all, even in sweet wines, and in larger quantities than one might be disposed to expect. In almost every case the free acids are more or less masked by sugar.

Under the term "free acids," I include the acid equivalent of cream of tartar and other soluble bitartrates found in wine, besides such acids as are quite uncombined, such as tartaric, malic, and acetic, and the insignificant amount of free tannic acid.

Flavour alone will not lead us to any just conclusions as to the amount of free acids in the wine, since a much smaller quantity is often found in acid wines, than in sweet ones, where the larger proportion of sugar conceals the free acids. In such a case, and, indeed, as a rule, the presence of a considerable quantity of free acid in any kind of wine with a proportionate amount of sugar, very materially improves the flavour of the wine.

To determine the quantity of free acid contained in wine is of sufficient importance for us now; we shall, therefore, reserve to a later period the question as to

what acids they are. A soda solution of a certain strength was used, and added drop by drop to the wine, till the acid reaction of the wine was completely destroyed, so that not only such acids as were quite uncombined, but half the acids of the acid salts were neutralized.

Güning, who has reckoned in anhydrous soda the amount of soda solution used, found in 100 C. C. wine, the following results in milligrammes of anhydrous soda (100 C. C. must not be taken at 100 grammes, for the sp. gr. of wine is never less than 0.990, and seldom exceeds 1.000, so that 100 C. C. represents from 99 to 100 grammes, but in a few kinds rises to 1.09, p. 167.)

Madeira	No. 1	213	No. 5	226	No. 9	232	} average 244
	2	232	6	225	10	288	
	3	220	7	244	11	232	
	4	267	8	251	12	263	
Teneriffe	No. 1	240	No. 5	220	No. 9	244	} average 231
	2	226	6	232	10	213	
	3	244	7	244	11	232	
	4	226	8	201	12	251	
Rhine wine	No. 1	263	No. 5	244	No. 9	257	} average 232
	2	261	6	230	10	244	
	3	197	7	191	11	226	
	4	226	8	213			
Port wine	No. 1	207	No. 5	209	No. 9	213	} average 188
	2	187	6	182	10	201	
	3	186	7	201	11	207	
	4	180	8	194			
Bordeaux ordinary	.	.	.	.	.	232	
Sauterne	.	.	.	.	.	238	



Burgundy Beaune . . . . .	194
Hermitage . . . . .	232
Lachryma Christi . . . . .	226
Muscat Rivesaltes . . . . .	226
Benicarlo . . . . .	307
Roussillon . . . . .	288
St. George . . . . .	269
Narbonne . . . . .	320
Tavella . . . . .	339
Langlade . . . . .	275
Cotes White . . . . .	256
Bergerac do. . . . .	288
Old Burgundy Pommard . . . . .	282
Grape-juice . . . . .	1,320

The grape-juice which we have made use of was procured from the purple grapes of our country, and is the same of which the extractive contents are given (p. 36). It must not therefore be looked upon as a standard for the juice of grapes from which wine can be prepared.

The amount of free acids in wine is that which can be saturated by means of soda or any other alkali: acetic acid has a place among them. It was distilled in an oil bath, and the liquid which distilled over was collected, and its acid contents examined with soda solution by Güning. Such wines among Madeira, Port, Teneriffe, and Rhine wines as gave an average amount of acid were selected.

I may here remark that some difficulty occurs in determining the volatile acids. Evaporation must not be allowed to proceed too far, otherwise even at 120° C. 248° F., part of the extractive matter would

be decomposed, and acetic acid formed. Wine extract is very easily decomposed. On the other hand, this extract retains acetic acid strongly. The following determinations were made with the necessary caution :

In 100 parts of wine a quantity of acetic acid, which sufficed to saturate the following amount of anhydrous soda in milligr. (.154 gr.) was found.

	Anhydrous Soda.	Acetic Acid in 100 grammes Wine.
Madeira . . . . .	310	167
Teneriffe . . . . .	70	114
Rhine wine . . . . .	41	66
Port wine . . . . .	58	95
Bordeaux ordinary . . . . .	53	86
Burgundy Beaune . . . . .	19	31
Bordeaux Sauterne . . . . .	54	88
Hermitage . . . . .	65	106
Lachryma Christi . . . . .	72	118
Muscat Rivesaltes . . . . .	52	85
Champagne . . . . .	39	64
Benicarlo . . . . .	57	93
Roussillon . . . . .	33	62
St. George . . . . .	79	129
Narbonne . . . . .	42	69
Tavella . . . . .	18	29
Langlade . . . . .	41	67
Cotes White . . . . .	77	126
Bergerac do. . . . .	83	135
Burgundy Pommard . . . . .	41	67 milligr.

Hence we see that from  $\frac{1}{4}$  to  $1\frac{3}{4}$  thousandth part anhydrous acetic acid is contained in wine. The smallest amount is found in Tavella, the largest in Madeira.

Now, if we call the other acids free tartaric acid (and for this purpose it may be allowed), then we can

easily calculate the amount of this tartaric acid from the quantity of soda which remains for saturation after what was necessary for the acetic acid has been deducted.

Hence we have tartaric acid  $C^4 H^2 O^5$ , in 100 grammes wine expressed in milligrammes.

Madeira . . . . .	102
Teneriffe . . . . .	351
Rhine wine . . . . .	480
Port wine . . . . .	283
Bordeaux ordinary . . . . .	390
Burgundy Beaune . . . . .	477
Bordeaux Sauterne . . . . .	207
Hermitage . . . . .	364
Lachryma Christi . . . . .	336
Muscat Rivesaltes . . . . .	357
Champagne . . . . .	408
Benicarlo . . . . .	545
Roussillon . . . . .	545
St. George . . . . .	414
Narbonne . . . . .	606
Tavella . . . . .	699
Langlade . . . . .	510
Cotes White . . . . .	390
Bergerac do. . . . .	448
Burgundy Pommard . . . . .	525

So that from 2 to 7 parts perfectly free tartaric acid are found in 1000 parts of wine. Tavella has the largest; and Bordeaux Sauterne the smallest amount. I must, however, remark that these last numbers are all too high, especially in the red wines, where tannic acid helps to saturate the soda solution, and where besides, another acid, of which we shall speak more particularly hereafter, appears in small quantities.

The quantity of acids in wine, that is, of acids with which alkali may be saturated, and which are perceptible to the taste, and to which the equivalent of tartaric acid, which is not combined with potash in wine, belongs, however insignificant it may be, is yet very variable. We have already made some mention of the amount of free acids (p. 176), in speaking of the different estimates of the alcoholic contents given by different analyses. Most of them, however, give no fixed quantity of acids, and do not even distinguish acetic from non-volatile acids. According to Lüdersdorff (p. 177), but very little difference exists between the French and Rhenish wines with respect to the total acid contents, while Fusenius (p. 178) considers that the best Rhine wines generally agree with one another, and contain about  $\frac{1}{2}$  per cent.

Dietz found in Rhine wines (p. 178) from 0.33 to 0.78 grammes potash necessary to saturate all the free acids: whilst Schubert found the maximum of free acid to be 0.45 and 1.35, and the average 0.8 and 0.9. Kersting (p. 183) found in the wines of the Bergstrasse from 0.6 to 0.8 free acids. It is particularly necessary to keep a distinction between acetic and tartaric acid, as the flavour of the wine very much depends on the preponderance of the one or the other. From the analyses that have been already made we learn that a considerable quantity of acetic acid is contained in all wines, and that their harsh flavour is by no means entirely to be ascribed to tartaric acid.

The question now is, whether any other free acids, besides tartaric, acetic, and tannic acid, exist in wine?

We must consider this point with attention. The acids may be either volatile or non-volatile.

I pass over the fatty acids, because we shall discuss them in treating of the odoriferous constituents of wine.

In the first place I must indicate malic acid, which is found free in Bordeaux, and, combined with lime, forms a salt easily soluble in water, insoluble in alcohol, and which may be obtained from the red wine, in which it is found by means of a process which will be described in the following chapter.

## CHAPTER XIV.

### MALIC, CITRIC, AND RACEMIC ACID.

It is scarcely necessary to draw attention to the tartaric and racemic acids in wine. Any one may convince himself of the presence of racemic acid by precipitating the wine with acetate of lead, suspending the precipitate in water, conducting sulphuretted hydrogen through it, filtering, and evaporating it. If a little chloride of calcium and ammonia be now added to the acids, but not enough of the latter to saturate them racemate of lime will be precipitated, and the further addition of ammonia will give rise to a precipitate of tartaric acid. A special investigation was necessary for the detection of citric and malic acid. There was indeed but little evidence of citric acid, though we examined red Bordeaux with the express purpose of discovering it.

Red Bordeaux was precipitated with sugar of lead, the deposit suspended in water, decomposed by means of sulphuretted hydrogen, and the sulphide of lead washed with water.

When milk of lime was added, all the acids remaining in the liquid separated from the sulphide of lead were saturated. Tartrate, racemate, and citrate of

lime remained insoluble, but malate of lime soluble. The insoluble lime salts were dissolved with muriatic acid, and ammonia was then added to them. This gave rise to a precipitate of tartrate of lime, and if racemic acid had been present racemate of lime would also have been deposited. Citrate of lime might still be present in the filtered liquid, but as no precipitate could be obtained by filtering and evaporating the ammonia, we infer that citric acid is not contained in wine. The liquid which flowed from the milk of lime was accurately saturated with acetic acid. It gave a precipitate with alcohol, which is a sign of the presence of malate of lime. Acetate of lead gave rise to a precipitate which is soluble in excess of acetate of lead, or when warmed, but separates again when boiled. A green liquid, but no precipitate, is obtained from it, by acetate of copper, whilst nitrate of silver and sub-nitrate of mercury gave a white precipitate; these reactions all indicated the presence of malic acid.

Since, however, the slight solubility of the lead salt prevented us from obtaining the malic acid, when the method described above was used, we adopted the following plan:—

Wine was digested with chalk upon a water bath till the acid reaction completely disappeared. The watery liquid was filtered and precipitated by means of alcohol.

The precipitate was dissolved again in water and re-precipitated by means of alcohol, and this process

was repeated several times, till it was sufficiently purified. The malate of lime would now be found in the precipitate with alcohol, but tannate of lime, gypsum, &c., might likewise exist. It was dissolved in water, sugar of lead added, and then filtered(*a*).

The precipitate, with acetate of lead, was then suspended in water, sulphuretted hydrogen conducted through it, the sulphide of lead filtered, the liquid warmed in order to expel sulphuretted hydrogen, and then cooled again: it was then fully saturated with milk of lime, the liquid filtered and neutralized with acetic acid. No tannic acid could be now found in it, but if malic acid exist in the wine, malate of lime was present.

All the tests which have been hitherto applied to malate of lime confirm its presence, and we therefore assume that a small quantity of malic acid is contained in red Bordeaux.

The liquid (*a*) which was separated from the precipitate of lead was first freed from lead by sulphuretted hydrogen; it contains a considerable amount of gum, which may be precipitated by alcohol. No copper could be reduced by the substance still remaining in the liquid, when a test solution of oxide of copper and potass was used, unless it had been previously warmed with hydrochloric acid, then a considerable precipitate was obtained. With the exception of acetate of lime, no other distinguishable substances remain in the liquid.



## CHAPTER XV.

### GLUCIC ACID.

THE experiments tried by Graham, Hoffmann, and Redwood, show that, besides carbonic acid and alcohol, another substance is formed during the fermentation of sugar which is no longer capable of fermenting, and is compared by them to glucic acid.\* By adding  $1\frac{1}{2}$ , 2, and 3 per cent., by volume, of wet yeast, to a solution of sugar, they obtained 4.4, 3.72, 3.7 per cent. of this substance, and more might have been procured, had a larger quantity of yeast been employed. By filtering and evaporating the liquid this substance was obtained as a dark brown matter, of the nature of extract, which had a bitter taste, and owing to the lactic acid contained in it, was acid. More than one substance was discovered in it, but no sugar, although it was able to reduce oxide of copper to a sub-oxide.

Thénard has already recognised this substance, and says, that when he allows sugar to ferment with a large quantity of yeast, he always obtained 4 per cent. of the sugar thus employed as an extractive matter.

\* Liebig u. Kopp, Jahresber, 1852, s. 801.

4 per cent. comes very near the 3·7 per cent. given by the above-mentioned chemists.

If glucic acid be really present in wine, and the wine be treated in the manner described (p. 248), the acid will be found in the liquid which has been filtered from the lime salt precipitated by alcohol. If the glucic acid be saturated with caustic potassa, it combines with it and forms a neutral salt, which is insoluble in alcohol; but if, as was the case here, it be saturated with chalk, an acid salt is formed, from which no precipitate can be formed by alcohol. The alcoholic liquid, separated from the neutral salt, contains not only all such acid glucate of lime as may be present, but likewise the sugar of the wine, nearly all the tannic acid, and such other substances as, under these circumstances, are soluble in alcohol.

The alcohol was distilled, the residue dissolved in water, and precipitated with basic acetate of lead, which gave rise to a copious precipitate.

After the lead had been removed from the liquid, which was drawn off, the presence of sugar was indicated by the copper test.

The precipitate of basic acetate of lead was suspended in water, sulphuretted hydrogen conducted through it, the liquid warmed in order to expel sulphuretted hydrogen again, milk of lime added in order to separate the tannic acid which was present in large quantity as a basic lime salt. The liquid was filtered, carbonic acid conducted through it, then warmed, and

again filtered in order to remove the chalk. If glucic acid were contained in the wine, we should find it here. Sugar could no longer exist. The liquid when warmed with test solution of oxide of copper and potash showed no reduction, therefore no glucic acid was found in red Bordeaux wines.

I do not, however, venture to assert that no glucic acid exists in wine; on the contrary, knowing how quickly and easily the sugar in wine (which is so liable to undergo change) may be resolved into glucic acid, I consider it highly probable it does exist. But glucic acid, even when combined with lime, may very easily be resolved into apoglucic acid, and then masked by the colouring matters of the wine. I shall speak again of this matter in treating of the decomposition of wine; I do not therefore deny that glucic acid is present in wine, but it is difficult to prove it.

## CHAPTER XVI.

### FORMIC AND LACTIC ACIDS.

THESE two acids have not yet been mentioned, for although their presence in wine may be justly suspected it has not yet been proved.

I have not been able to detect formic acid in Port, Madeira or Teneriffe wines by distillation, and when nitrate of silver and a little ammonia were added to the distillate no silver was reduced. No brown colour was produced by means of caustic potash, so we may conclude that no aldehyde is present in it.

With respect to lactic acid, lactate of lead is soluble. Lactic acid must therefore be sought in the liquid obtained by precipitating the wine with sugar of lead, basic acetate of lead, and ammonia, and then filtering.

When this liquid (obtained from red Bordeaux) has been freed from lead by sulphuretted hydrogen, filtered and evaporated, the residue is easily soluble in alcohol. This deposit, in which there was a good deal of sugar, was digested with carbonate of zinc upon a water bath, and freed with alcohol from sugar and

other ingredients. The residuum, which was soluble in alcohol, was treated with warm water. If lactate of zinc were present it would be found in the watery solution. None was found, and hence we infer that not even a trace of lactic acid exists in red Bordeaux.

## CHAPTER XVII.

### ALBUMINOUS MATTER.

WE have seen that albuminous matter is contained, not only in grape-juice, but in the juice of every other fruit; we know that the fermentation of grape-juice must be caused by an albuminous body; we have learnt that during fermentation the albuminous matters of the grape-juice and pulp are resolved into ferment, and are separated in the form of an insoluble body, of which, according to Braconnot, as much as 20·7 per cent. may be found in the sediment of newly-made wine.

We must not, however, infer from this that no albuminous body in any form can be found in wine, but only conclude that but little of any kind of albumen will exist in it.

If we remember further that tannic acid is found in red wines, and that this acid has a chemical attraction for albumen, we shall see that the largest quantity of albuminous matter will not be found in red wines containing much tannic acid.

And besides this, alcohol, even when much diluted with water, is able to precipitate most albuminous

bodies ; and they will, therefore, be found but sparingly in wines containing much alcohol.

In opposition to this, we must consider that albumen is soluble in tartaric acid, even when alcohol and tannic acid co-exist. These last two substances render albumen insoluble, but tartaric acid neutralises their action, and retains the albumen in solution, and the more easily the larger the proportion of water in the liquid. The free tartaric acid contained in wine renders it possible for an albuminous body to exist in it in a soluble form, if any is left from the previous fermentation.

If no tannic acid and but little alcohol exist in any fermented liquid, no tartaric acid will be required to keep the albumen in a state of solution. This is proved by beer, in which a considerable quantity of albumen may be dissolved ; for freshly-drawn beer, though frothy and clear as water when poured out, soon deposits a very considerable sediment of newly-formed ferment.

I drew attention to this fact (p. 144) as it occurs in Champagne and other effervescing wines, in which, after the clear wine has been poured out, ferment is formed, which sufficiently proves that albumen exists in them.

I may here mention that many of the wines I have examined contain a perceptible though small amount of albumen ; perceptible, that is, if chlorine water be dropped into liqueur wine. This gives rise to a

flocculent precipitate possessing all the properties of a compound of chlorine and albumen (albumen-chloride).

As in many wines which have not been subjected to evaporation this precipitate is not observed, it is difficult to determine the amount of albumen present in wine by weight. Still I consider the determination by no means unnecessary. Liebig entirely denies the presence of albumen in wine, and yet the quantity contained in it is such that it can hardly escape the examiner, though in Madeira and Teneriffe the amount is certainly small. If chlorine be conducted through fresh grape-juice which has been filtered, and in which the presence of free tartaric acid has prevented the albumen from coagulating by heat, a copious precipitate of chloride of albumen will be the result, which agrees entirely with the statements already made in treating of grape-juice (p. 37).

Considering the matter dietetically, the presence of this trace of albumen in wine might be completely disregarded, and I have not yet been able to ascertain the exact nature of the albuminous body indicated by such traces. We may assume that it arises under the influences of ferment, and therefore no longer belongs to the unaltered albuminous bodies which appear in the plant itself.

I should not dwell so long on the existence of this trace of albuminous matter, were not its presence of importance on two accounts—first, that it gives us



one more means of detecting adulteration when wines are analysed with this view.

This ingredient may, however, like many other components of wine, be imitated, and yet, any one undertaking to imitate artificially the quantity (be it smaller or greater) of albumen precipitable by chlorine, and peculiar to every kind of wine, would encounter great difficulties.

Wine prepared from the juice of other fruits will give too much or too little albumen, and other varieties will occur in wines imitated in a different manner—in some, perhaps, to the complete exclusion of albuminous matter. The quantity of albumen rightly belonging to each kind of wine may be easily learned by determining what is present in genuine wine.

The second point which causes the presence of any albumen to be considered important, is its capability of spoiling wine, since all albuminous bodies undergo chemical change, and are capable of transferring this motion to such other bodies as may be brought into contact with them.

Alcohol hinders such changes, which are less to be expected in strong wines. But albumen effects changes even in alcohol, which if air be admitted it oxidises, and turns into acetic acid; and it even makes wine mouldy, *i. e.* changes the alcohol which had previously been converted into acetic acid, or not, as the case might be, into vegetable gluten and

mould plants, that is, into cellulose. And albumen is necessary, though in but small quantities, to the formation of acetic acid from alcohol, and also of mould. If no trace of albumen were found in the wine, it would be impossible that any mould fungi, whose existence depends upon albumen, should be produced in wine in so short a time, as occasionally occurs.

A considerable quantity of albumen is by no means injurious to wines containing much tannic acid and alcohol, since both these substances check the decomposing action of albumen; but in wines containing little tannic acid and alcohol, such, for instance, as the less excellent Rhine wines, the small quantity of albumen contained in them continues to act upon the other ingredients so as to produce decomposition, and such wines will not, therefore, keep long. Such Rhine wines as are able to defy time are richer in alcohol, and those sweet wines which contain a great deal of sugar, possess in that sugar an element which hinders the action of albumen. Sugar may generally be employed to preserve such substances as abound in albumen from spoiling. Excess of sugar, brought into contact with a small portion of albuminous matter, checks its action, as do also alcohol and tannic acid.

In conclusion, I must observe, that nitric acid does not precipitate albumen out of wine, but it is found in the copious precipitate caused in wine by acetate of lead.

If the albuminous matter present in wine be small, such components of ferment as are soluble in weak spirit, will be found in great abundance, for out of the albumen much ferment has been formed, and this gives its soluble constituents to the wine. In other words, what we have hitherto called ferment extract, may exist in the wine, so much at least as is not precipitated by alcohol.

This ferment extract, if obtained by treating ferment with cold water, is insoluble in alcohol,\* and not quite insoluble in weak spirit. It is a substance which has lost every characteristic by which albuminous bodies are distinguished, but may be precipitated by tannic acid, or mineral acids.

I found this extract to have the following composition in four different kinds of ferment:

	I.	II.	III.	IV.	Albumen.
C. ....	43·4	47·0	46·4	45·6	53·5
H. ....	6·6	6·3	6·7	6·5	7·0
N. ....	12·7	10·6	12·7	11·7	15·5
O. ....	37·3	36·1	34·2	36·2	22·0
S. Ph. ....	—	—	—	—	2·0

I have added the composition of albumen as found in eggs, in order to show how great the difference is between this ferment extract and albumen and vegetable gluten. The amount of oxygen is much increased.

But the substance which is here exhibited in an impure state, as the figures prove, is unknown to us

\* Scheik. Onderz. d. II. p. 458.

pure, since it is a mixture of various ingredients, and we only know that it must be found in wine in small quantities.

To determine the composition of the albuminous matter of wine, or the ingredients of the ferment extract which appear in it, would be a very expensive undertaking. I have not attempted it, but depending on the determination given by Vlaanderen respecting the nitrogenous contents of wine extract, I feel myself competent to give an opinion as to the quantity of these substances existing in wine.

The wines mentioned below were used for this purpose; being allowed to evaporate, and the residue dried at 110 C., 230° F., after which the amount of nitrogen was determined according to the method pursued by Will and Varrentrapp.—Benicarlo:—1.734 gave 0.105 platina. In 100 parts of wine 2.87 extract was found, which gives 0.026 nitrogen in 100 parts wine. Roussillon, 1.375 gave 0.0985 platina. There is 3.11 extract, which gives 0.029 nitrogen in 100 parts of wine. St. George, 0.849 gave 0.063 platina; 1.81 extract, consequently 0.020 nitrogen in 100 parts wine.

Narbonne, 1.079 gave 0.072 platina; 2.20 extract, and 0.021 nitrogen in 100 parts of wine.

White Côtes, 0.657 gave 0.074 platina, 1.48 extract, that is, 0.023 nitrogen in 100 parts of wine.

Old Burgundy-Pommard, 0.991 gave 0.157 platina; 1.80 extract, and 0.40 nitrogen in 100 parts of wine.

This nitrogen may either belong to ferment extract or to a compound of ammonia, the quantity of which must, however, be exceedingly small, or it may belong to some albuminous substance.

If we reckon all this as albumen, and this at 15.5 per cent. nitrogen, we may calculate the albumen in 10,000 parts wine, or we may take it as ferment extract, and reckon 12 per cent. nitrogen.

	Albuminous bodies.	or	Ferment extract.
Benicarlo .....	17		22
Roussillon.....	19		24
St. George.....	13		16
Narbonne .....	14		17
White Côtes .....	15		19
Bourgogne Pommard ....	26		33

That is, from  $1\frac{1}{2}$  to  $2\frac{1}{2}$  parts albumen, or from  $1\frac{1}{2}$  to 3 parts ferment extract in 1000 parts wine.

The amount of nitrogen arising from ammonia, or other nitrogenous substances found in wine, must be subtracted from this estimate. But this amount is a minimum, though singularly enough it varies but little in quantity.

## CHAPTER XVIII.

### ŒNANTHIN—(GUM).

UNDER this title Fauré first described a substance which he maintains he found in the best French wines. To this he ascribes the substance and body of the wine, a property which is highly valued in good Médoc wines. The œnanthin itself is described by Fauré as viscid, ropy, and elastic, soluble in water and weak spirit, dissolves when exposed to warmth, swells if the heat be great, and then yields ammonia. It can no more be precipitated by solution of tannic acid, than by boiling in water, nor does it render the water acid. Mineral acids colour it without much altering its properties. Sulphuric acid does not resolve it into sugar, nor can nitric acid convert it into mucic or oxalic acid.

Fauré did not find this substance in indifferent wines, it was found in small quantities in moderately good wines, but in the best wines it always appeared, though in very variable quantities.

Œnanthin exercises a very great influence upon the flavour of the wine; aromatic wines in which it is wanting are on that account less palatable, which is

proved by the fact that their flavour is greatly improved by the addition of cœnanthin.

Fauré, in order to obtain this cœnanthin, precipitates the colouring matter and tannic acid with isinglass, evaporates the colourless extract to the thickness of extract, dissolves the extract in alcohol of 85 per cent. which takes up such substances as have escaped the isinglass, whilst the cœnanthin collects together as a sticky mass, it is re-dissolved in weak alcohol and precipitated by alcohol of 85 per cent.

We have already given Fauré's estimate of the amount of cœnanthin in different wines. (P. 172.)

In preparing cœnanthin in the manner previously recommended difficulties will occur. It is, for example, impossible to free red wine from colouring matter by means of isinglass or albumen, or even by boiling it in excess of albumen. The wine becomes very pale, but not colourless. Nor is it possible to render the wine perfectly colourless by adding isinglass and tannic acid. The reason of this is very clear, the colouring matter of wine does not combine with isinglass or albumen, but clings to them; and as it is soluble in weak alcohol and tartaric acid it is partially dissolved, and it cannot be included in a coagulum of tannic acid and isinglass, or albumen, even when it is coagulated by boiling.

But if wine cannot be freed from colouring matter by isinglass, as was known, indeed, to Fauré, it is equally useless to precipitate the wine first with isin-

glass in order to prepare its œnanthin; particularly as Fauré is convinced that œnanthin cannot be precipitated by tannic acid which is soluble in alcohol, in which œnanthin is insoluble.

Besides this, it is extremely difficult, if not impossible, to add only just so much isinglass as is necessary to precipitate tannic acid; an excess would adulterate the œnanthin with gelatine.

Disregarding, therefore, his suggestions, I evaporated the wine, precipitated the residue with alcohol, dissolved the precipitate in water, and re-precipitated it in alcohol, and this process I repeated several times.

I obtained every time a powdery precipitate, and as the colour was principally absorbed by the spirit it became paler every time.

From this powdery precipitate a coherent mass could be collected, whilst the crystalline precipitate of the salts again separated a quantity of viscid matter which was again obtained when the crystalline precipitate was re-dissolved in a little water, and precipitated with a little alcohol.

As soon as the viscid substance was obtained it was purified, that is, it was dissolved in a little water, and a little alcohol added to free it as much as possible from the salts, tannic acid, and colouring matter which were mixed with it. After this treatment had been repeated several times, it was as pure as it is possible to procure it in this manner.

The quantity of œnanthin found in ordinary Bor-



deaux is considerable enough to be looked on as one of the ingredients of red wine, and the peculiar characteristic assigned to it by Fauré cannot be admitted, namely, that the greater consistence which marks old wines, or which have been long in cellar, arises from it.

It is soluble in water, but not in alcohol, in which liquid, if left for a time, it loses its clamminess, softness, and coherence, and becomes hard and brittle, but if soaked in water regains its viscosity. Cœnanthin cannot be precipitated by tannic acid.

Unlike Fauré I discovered no nitrogen in it. If subjected to dry distillation it gives rise to a strongly acid liquid which, if saturated with potash and touched with a rod wetted with muriatic acid, exhibits only a very faint trace of ammonia.

I have been at great pains to ascertain these facts, and we are now sure that the substance before us is neither albumen nor vegetable gluten, nor one of their nitrogenous products. Neither albumen nor vegetable gluten can appear in it, for they are soluble in alcohol and tartaric acid, and there was only a trace of a substance yielding ammonia, and this did not belong to the chief substance present. I, like Fauré, found the substance easily soluble in boiling water, and not coagulatable by heat. But its transformation into sugar when warmed with sulphuric or muriatic acid, contradicts his assertions, and is an ascertained fact. Cœnanthin is, as we have seen, a

mixed substance, and yields when warmed with diluted sulphuric or muriatic acid and mixed with test solution of oxide of copper and potass, a considerable amount of sub-oxide of copper.

The method of preparation described above gives us the cœnanthin substance in a very impure state, since it is impossible by such means to get rid of all cream of tartar and other such vinous ingredients as are soluble in water and insoluble in alcohol. In order to obtain it pure, it was dissolved in water and filtered, and acetate of lead was added to a portion of it. This gave rise to a copious precipitate, in which, among other components, tartrate of lead was contained. The liquid which passed through the filter was precipitated with alcohol, for it still retained what Fauré calls cœnanthin. But little precipitate was obtained by basic acetate of lead from the watery fluid which flowed from the sugar of lead, but the addition of ammonia gave rise to a copious precipitate. These are the properties peculiar to gum, dextrin, or vegetable mucus, which may all be precipitated by alcohol, and easily resolved into sugar, in one word, they have the reaction of so-called cœnanthin. In order to be sure whether the cœnanthin mentioned by Fauré, in a pure state, was vegetable mucus or a gummy substance resembling dextrin, its solution was warmed with test solution of oxide of copper and potass. (This cœnanthin solution can easily be obtained pure by passing sulphuretted hydrogen through the liquid which

flows from the precipitate with sugar of lead, evaporating it and extracting it with alcohol, in order to dissolve the acetate of potash). It was immediately reduced to suboxide of copper, without being previously transformed into sugar, by being warmed with an acid.

There is, therefore, no quality peculiar to gum or dextrin, which may not be likewise discovered in the pure cœnanthin described by Fauré. When in the impure state, in which it was when prepared by Fauré, it is a mixture of different bodies; and we cannot, therefore, allow this substance a place in science as a distinct and peculiar body.

I cannot undertake to decide whether it should be called gum, vegetable mucus, or dextrin, its sliminess and coherence give it the character of vegetable mucus; its easy solubility in water causes it to resemble gum; its power of reducing oxide of copper is like dextrin. We know that there are as many kinds of gum as sorts of sugar; the name is indifferent, if the nature of the substance be sufficiently understood.

We must remember that one kind of gum has already been mentioned (p. 248) as existing in wine, which does not reduce the copper in a test solution of oxide of copper and potass, unless it has previously been resolved into sugar by muriatic acid. It was therefore a question whether two kinds of gum existed in wine, one which had the reaction of dextrin

with the copper test, and another which does not give this reaction till it has been resolved into sugar by the action of an acid. To this question I reply in the negative. The gum of which we spoke (p. 248) was obtained by evaporating wine with chalk, that is, by saturating the free acids; whilst the œnanthin described by Fauré is obtained from the evaporation of wines alone, and therefore it is exposed to the influence of free acids and heat. The gum mentioned (p. 248), when treated with sulphuric acid and heat, is resolved in a few minutes into sugar. Solution of gum arabic, when exposed for a short time to heat, and acted upon by tartaric acid, passed into dextrin, and afterwards into grape sugar; so also the gum of wine, which has been evaporated with tartaric acid, will be found resolved into dextrin.

There is therefore no ground for assuming that two kinds of gum are present in wine. The gum of wine when prepared, according to Fauré's method, has the reaction of dextrin, but when separated by chalk, that is, in the unaltered form in which it actually appears in wine, it shows no reaction of dextrin, and cannot be justly called by that name.

With respect to the amount of gum which, according to Fauré, is greater in old cellared wines than in young ones, this fact, even if proved (which it is not, since he worked with a very impure substance), would be either the consequence of a gradual resolution of the sugar of wine into gum,

which resolution is speedily effected, when the wine becomes ropy (p. 127); or of the transformation of tartaric acid into gum, or vegetable mucus (p. 114).

It cannot be denied that some cellared wines increase in consistency and sweetness till they resemble syrup. This change may be effected by a large amount of gum or vegetable mucus, and if these substances are really formed from tartaric acid, we have discovered how it is that wine becomes sweeter and more consistent.

The subject is sufficiently important to deserve examination, although we can hardly expect that an analysis of wine will make us accurately acquainted with it; for supposing a larger quantity of gum to be found in old than in young wines, which considering their greater consistence is not improbable, who can assure us that the old wines did not originally contain a larger proportion of gum?

That vegetable mucus is produced from sugar, and cellulose from tartaric acid, is well known, and the approximation in kind, and identity in combination of cellulose, and vegetable mucus or gum, and the decrease in acidity of old wines is equally acknowledged. I alluded to the diminution of acids in wine (p. 113); as regards the chemical composition of these substances, it would make no difference whether sugar or gum were formed.

## CHAPTER XIX.

### AMMONIA OR AMMONIACAL SALTS.

THE fact that a considerable portion of albuminous matter which had previously passed into ferment, is decomposed during the fermentation of wine, leads us to expect with more or less certainty the presence of ammonia combined with some acid in wine. No ammonia is to be found in grape-juice, and if it appears in wine it must be as a product of decomposed albuminous matter.

In two kinds of wine, Rhine and Teneriffe, which I examined by mixing them with potash, and then testing them with a rod moistened with muriatic acid, I have invariably found an insignificant trace of ammonia, but very great care was required to place its existence beyond a doubt; in Port wine and Madeira not the smallest vestige of it could be detected.

Since Rhine wines are so constituted as to be more disposed to slow decomposition in consequence of the resolution of albuminous matters, than stronger wines, and only very faint traces of ammonia are discernible, we may safely assume its importance in wine to be quite secondary.

If wine be evaporated upon a water bath, and concentrated to the thickness of syrup, the addition of potash will always develop traces of ammonia, of whatever kind the wine may be; but the quantity nevertheless appears to be very insignificant.

Döbereiner endeavoured in another way to determine the presence of ammonia in wine, by distilling the wine with potash, and adding chloride of platinum to the distilled liquid. In the wines thus examined by him, he detected ammonia; but this method only indicates the presence of a nitrogenous substance, which yields ammonia when treated with potash; and such are both albumen and ferment extract, and the existence of actual ammonia is by no means proved.

P. 60, we mentioned a test used by De Saussure, which required 0·81 grammes (12·5 grs.) of ammonia to saturate the acids in 375 grammes (5787·7 grs.) of must, whilst only 0·76 grammes (11·7 grs.) of ammonia were necessary to neutralise the same quantity of must, when it had been allowed to ferment in a vacuum. The difference here = 0·05 (·8 grs.) is insignificant, but De Saussure, like Döbereiner, ascribes it to the formation of ammonia which they think occurs during fermentation.

If now any one should imagine that during the decomposition of the ferment of 375 grammes of must, no more ammonia could be formed than is contained in 0·05 grammes of sal-ammoniac, he would be much mistaken. It was necessary to add 0·81 ammonia to

the fresh must in order to neutralise the tartaric acid of the must. This acid continued to exist. If now, acetic or any other organic acid should be formed in the vacuum, then as much as at least 0.05 grammes ammonia more might be formed by the decomposition of ferment, so that the liquid after fermentation would have a less acid reaction than before it was tested.

Hence from De Saussure's test we must not conclude that no ammonia is formed during fermentation; on the contrary, we have seen that it really is produced (p. 67). But as phosphoric acid and magnesia exist in grape-juice, the ammonia immediately after its formation is separated out of the fermenting juice as phosphate of ammonia and magnesia.



## CHAPTER XX.

### ODORIFEROUS VOLATILE ALKALI OF WINCKLER.

AROMATIC wines contain, according to Winckler, not only acids, and compounds of ethyl with acids, but also a substance of an alkaline nature, to which he principally ascribes their aroma. We find this substance mentioned in the Journ. de Pharm. tom. xxiii. p. 374; and at p. 469 an extract is given from Winckler's works, "Beiträge zur genauen kenntniss der chemischen Constitution des Weines, Landau, 1852."

The matter may be shortly stated as follows :

Winckler distilled off all the volatile substances of wine, mixed the residue with water and unslaked lime, and re-distilled it, taking care to have the receivers well cooled. The volatile base which passes over has a strong alkaline reaction, neutralizes acids, and possesses, in a high degree, the smell of wine.

By filtering the liquid which remained in the retort, and saturating it with sulphuric acid, he obtained from the distillation a volatile acid, which had a very agreeable smell, and when mixed in right proportion with the volatile base restores to it the vinous aroma.

Although the editors of the "Journal de Pharmacie" drew our attention to these facts for two consecutive months, we may venture to agree with them in their last publication in doubting them.

Our researches have been prosecuted in the manner suggested by Winckler.

Günning (who is now endeavouring to discover the origin of raisin vinegar) first obtained an alcohol, the smell of which was almost insupportable, by distilling fermented raisin juice with lime; this alcohol had a strongly alkaline reaction, and plainly indicated, when touched with a rod wetted with muriatic acid, that it contained either ammonia or volatile alkali. It was saturated with muriatic acid and evaporated, and during evaporation it lost a little of its colour. Crystals of some salt remained, which were dissolved in water and mixed with chloride of platinum, ether and alcohol. The precipitate obtained was apparently ammonio-chloride of platinum.

The dried residue, when burnt, emits an odour which distinctly indicates ammonia, and 0.0276 of it yielded 0.0114 platinum; ammonia would yield 0.0113 platinum.

As was to be expected, ammonia was liberated from the albuminous liquid of the fermented raisins by distillation with lime.

Oudemans, following Winckler, has endeavoured to discover a volatile odoriferous alkali. He evaporated red Bordeaux, and added quick lime to the water that

distilled over. By re-distilling this a foetid liquid was obtained, which had a strongly alkaline reaction, and evidenced, when tested with a rod wetted with muriatic acid, the presence of a considerable amount of ammonia or some other volatile base.

The liquid was now neutralised with muriatic acid and evaporated, crystals of salt were left, which were dissolved in water, mixed with chloride of platinum, ether, and alcohol, and filtered; then washed with ether and alcohol, and dried at  $100^{\circ}$  C. ( $212^{\circ}$  F.), and 0.0165 of this gave 0.0074 platinum.

Ammonia would give 0.0073, so the volatile alkali in this wine is ammonia.

The wine was pure Bordeaux, and had an agreeable smell and flavour.

These tests appear to me sufficient to render any further research after the odoriferous volatile alkali in wine unnecessary. With the ammonia a little of some odoriferous substance may distil over from the wine, but the alkali is always ammonia.

## CHAPTER XXI.

### SUGAR IN WINE.

Two methods have been adopted for determining the saccharine contents of wine; the wine has either been freed from alcohol by evaporation, ferment added to the residue, and the amount of sugar calculated from the loss of carbonic acid during fermentation (Fresenius), or it is treated in the manner already prescribed for determining grape sugar, by a standard solution of salt of oxide of copper. Fehling, who has repeatedly tried this latter method, remarks, that it gives from  $\frac{1}{4}$  to  $\frac{1}{2}$  per cent. too much sugar, since there are other substances besides sugar in wine, which reduce the oxide of copper to a sub-oxide. I never directly examined the saccharine contents of wine, as they have been sufficiently analysed by others; who, however, using a solution of copper, always obtained a constant error to the amount just mentioned (since there are bodies in wines besides sugar, which reduce oxide of copper to sub-oxide); and by the method of fermentation a mistake of 4 per cent. may be caused, as is mentioned by Thénard (p. 251).

Besides this, the saccharine contents of wine may be approximatively estimated from the wine extract.

We have taken Fresenius' determination as our rule (p. 178), and not those given by Fischern (p. 178), since he, in common with Deitz (179), and Kersting (183), gives too low an estimate. According to Fresenius the sugar in four kinds of Rhine wine amounts to exactly six-sevenths of the extract, which gives, in seven parts residue, six parts sugar and one part composed of all the salts and non-volatile substances.

This is true of Rhine wines, but in red Bordeaux very little sugar is found. Not 1 per cent. extract is found in Bordeaux Sauterne (red), in Hermitage 1.7 per cent. extract. If then one-third of this be sugar, it would give one-half per cent. sugar. In Muscat Rivesaltes  $24\frac{1}{2}$  per cent. extract are found, 22 per cent., or more, of which are perhaps sugar.

In order to give a complete view of the saccharine contents of wine, I refer to the passages quoted above, and to what will follow immediately upon wine extract.

To determine the sugar in red wine it is necessary either to remove the colouring matter by means of acetate of lead, or completely to discolour the wine by means of animal charcoal, which must then be washed. This latter expedient completely answers the purpose. The sugar which appears in wine has the distinctive characteristics of uncrystallisable sugar, as it is produced under the influence of fermentation; the grape sugar of grapes passes first into fruit sugar, and then into uncrystallisable sugar.

However insignificant the amount of sugar may

appear in some wines, it is nevertheless of great importance both in diminishing the sharp taste of the free acids, and in imparting an agreeable flavour to the wine.

Unless red wines contain about half per cent. sugar, their flavour is not agreeable; in some the quantity is more considerable.

Sweet wines, some of which owe nearly one-fourth of their weight to sugar, often contain not only a little uncrystallisable sugar, but fruit sugar.

## CHAPTER XXII.

### NON-VOLATILE CONSTITUENTS OF WINE.

IF wine be evaporated to dryness, a certain amount of solid substances is always left, which invariably acquires a darker colour if dried at a temperature of 110° C. 230° F. All such ingredients as are volatile, as ether, or volatile oil, besides alcohol and water, then disappear, whilst the sugar, gum, albuminous matters, extractive matters (still imperfectly known), the non-volatile free acids, the salts of organic and inorganic acids are left.

The following amount of these substances added together, is given by Vlaanderen after drying 100 C. C. wine at 110°, 230° F. until it ceased to lose weight (which is effected slowly).

Madeira .	No. 1	4.38	No. 5	3.49	No. 9	3.83	} average 4.02
	2	3.63	6	3.75	10	4.21	
	3	3.71	7	4.54	11	4.34	
	4	4.04	8	3.85	12	4.43	
Teneriffe .	No. 1	3.36	No. 5	3.18	No. 9	3.73	} average 3.26
	2	2.84	6	3.41	10	2.93	
	3	3.51	7	2.85	11	2.98	
	4	3.08	8	3.56	12	3.45	
Rhine wine	No. 1	1.94	No. 5	1.58	No. 9	2.15	} average 1.77
	2	2.11	6	1.45	10	1.56	
	3	2.00	7	1.61	11	1.83	
	4	1.33	8	1.90			

Port wine .	No. 1	4·87	No. 5	4·35	No. 9	5·24	} average 4·45
	2	4·15	6	4·45	10	4·46	
	3	4·37	7	3·93	11	4·40	
	4	3·75	8	5·00			
Bordeaux .	.	.	.	.	.	1·64	
Burgundy Beaune .	.	.	.	.	.	1·41	
Bordeaux Sauterne .	.	.	.	.	.	0·95	
Hermitage .	.	.	.	.	.	1·72	
Lachryma Christi .	.	.	.	.	.	20·12	
Muscat Rivesaltes .	.	.	.	.	.	24·52	
Champagne .	.	.	.	.	.	8·27	
Benicarlo .	.	.	.	.	.	3·11	
Roussillon .	.	.	.	.	.	2·87	
St. George .	.	.	.	.	.	1·81	
Narbonne .	.	.	.	.	.	2·20	
Tavella .	.	.	.	.	.	1·85	
Langlade .	.	.	.	.	.	1·40	
Côtes (white) .	.	.	.	.	.	1·48	
Bergerac (white) .	.	.	.	.	.	26·81	
Burgundy Pommard .	.	.	.	.	.	1·80	

The quantities given as remaining after evaporation and drying at 110° C. 230° F., do not entirely agree with those which have been found by others; but as it is extremely difficult to obtain these residuary substances quite free from water, we may question whether all analysers have dried them as carefully.

In the following list of wines the quantity of dissolved and non-volatile substances found in 100 grammes is expressed in grammes, (15·4 grs.)

French wine.	Château Margaux	.	.	.	2·60	Joss.*
"	St. Estèphe .	.	.	.	3·21	"
Wine from Greece	.	.	.	.	4·76	"
"	Sicily. Marsala	.	.	.	4·50	"
"	the Palatinate, Bavaria,	maximum				
"	from 16 kinds	.	.	.	3·60	Zierl.*
"	"	"	minimum		1·99	"

\* Halymetrically, and therefore inaccurately determined.



French wines . . . . .	average .	2.2	Bouchardat.
" . . . . .	maximum	2.8	Filhol.
" . . . . .	minimum	1.9	"
Austrian wines . . . . .	maximum	9.6	Hitchcock.
" . . . . .	minimum	1.4	"
French wines . . . . .	maximum	2.0	Lüdersdorff
" . . . . .	minimum	1.8	"
Rhine wines . . . . .	maximum	2.3	"
" . . . . .	minimum	1.5	"
Tokay . . . . .	. . . . .	10.6	"
Malaga . . . . .	maximum	18.7	Mayer.
" . . . . .	minimum	14.4	"
Rhine wines . . . . .	maximum	10.6	Fresenius.
" . . . . .	minimum	4.2	"
Bergstrasse . . . . .	maximum	1.6	Kersting.
" . . . . .	minimum	0.8	"
Rhine wines . . . . .	maximum	3.2	Diez.
" . . . . .	minimum	2.0	"
" . . . . .	maximum	9.9	Geiger.
" . . . . .	minimum	2.2	"
Palatinate wine . . . . .	maximum	10.7	Fischern.
" . . . . .	minimum	1.9	"
Wurzburg . . . . .	maximum	7.2	Schubert.
" . . . . .	minimum	1.1	"
Département du Lot. . . . .	maximum	4.9	Clary.
" . . . . .	minimum	4.0	"
Tokay . . . . .	. . . . .	10.0	Knapp.

The flavour of wine is without doubt very much affected by the residue left after evaporation, which contains fixed and free acids, of different kinds, besides sugar; the acetic acid, together with alcohol, water, and the odoriferous constituents, has evaporated, but the tartaric acid and cream of tartar remain, as do also the tartrate and phosphate of lime, phosphate of magnesia, the trace of gypsum, or sulphate of lime, and a trace of common salt. Taken together, they have not much taste; but probably have some

effect on the taste of the wine; whilst the influence of the colouring matter of red wine and of the apothema of tannic acid is less decided; on the other hand, the tannic acid, especially in the red wines, has a decided influence on the taste of the wine. However small the quantity of gum may be, it serves when combined with sugar to soften a little the sharp taste of the acids; the albumen is of no importance to the flavour.

Lastly, only three substances are left; first, the extractive matter which is present in the grapes, a substance which appears in many plants, is found in all parts of the plant, and may be so prepared as to serve for medical purposes as an extract, or may be chemically determined by evaporating a watery extract. Secondly, a soluble substance formed during the decomposition of ferment. Thirdly, a substance which remains over during the saccharine fermentation, and invariably succeeds, however great the quantity of ferment may be in withdrawing a portion of sugar from its influence. We have already spoken of all these substances, and have now only to consider the wines with a view to that which is left after evaporation, so as the better to compare them.

The sweetest wines leave the largest residue after evaporation; it amounts sometimes to one-fourth of their weight.

Besides these, ordinary Rhine and French wines differ but little in the total amount of solid matter; they contain on an average 2 per cent. The better wines, on the contrary, contain as a rule more, in

consequence of the evaporation they underwent whilst in cask. The amount in Madeira and Teneriffe may rise to 3, 4, or 5 per cent., in Port to  $4\frac{1}{2}$  or 5. In good cellared Rhine wines it may rise from 2 to 10 per cent.

All the substances found in the extract, taken collectively, materially promote the excellence of the wine.

I have purposely made no attempt to answer the question so frequently and so uselessly put, "Why one kind of wine is better than another?" Every constituent helps to promote excellence; alcoholic contents, bouquet, and every non-volatile ingredient. One wine is liked on account of its aroma (and when we consider the connexion between nose and mouth, aroma is flavour); another on account of its strength; a third simply because of its flavour. The importance of a considerable amount of non-volatile ingredients in wine is taught us by the intimate connexion between the value attached to certain wines, and the amount of the so-called wine extract. But it is not a standard, for different people use different measures.

I may here insert a remark upon the value of a very simple method, which has been suggested for determining the amount of wine extract, from the specific gravity of wine which has been freed from alcohol by evaporation, and restored to its original volume by means of water. If this be so, then the areometer, or anything else by which the specific gravity can be determined, would equally determine the amount of substances left after evaporation, which

would render the process much easier than it is, for evaporation is always a very tedious process. The wine extract dries slowly, and it must not be forgotten, that during evaporation it acquires colour, so that not even the greatest care can ensure a pure result.

The method used was this—a certain quantity of sugar was dissolved in a certain proportion of water, the specific gravity was then determined, so that by determining the specific gravity of another liquid in which an indefinite quantity of sugar is contained the amount of sugar in the unknown solution might be ascertained; that is, a scale of sugar is formed.

Balling\* has shown in detail that a solution of sugar and a solution of wine or beer extract, when they have the same specific gravity, contain like quantities of sugar or extract, and that in the following proportions, at 17° 5 C., 63·5° F.

Sp. gr.	Sugar or extract per cent.	Sp. gr.	Sugar or extract per cent.
1·000 . . . . .	0	1·053 . . . . .	13
1·004 . . . . .	1	1·057 . . . . .	14
1·008 . . . . .	2	1·061 . . . . .	15
1·012 . . . . .	3	1·066 . . . . .	16
1·016 . . . . .	4	1·070 . . . . .	17
1·020 . . . . .	5	1·074 . . . . .	18
1·024 . . . . .	6	1·079 . . . . .	19
1·028 . . . . .	7	1·083 . . . . .	20
1·032 . . . . .	8	1·088 . . . . .	21
1·036 . . . . .	9	1·092 . . . . .	22
1·040 . . . . .	10	1·097 . . . . .	23
1·045 . . . . .	11	1·101 . . . . .	24
1·049 . . . . .	12		

\* Gährungs-chemie, end of the first volume.

We will now select a few examples of extract obtained by direct evaporation and weighing.

Madeira, freed from water and alcohol, and restored by water alone to its original volume, has a specific weight of from 1·0169 to 1·0192 (p. 165). According to Balling, we should find in this from 4·25 to 4·75 per cent., and we find 3·64—4·54 (p. 281); Teneriffe, freed from alcohol, has a specific gravity of from 1·0122 to 1·0164 (p. 165). This, according to Balling, must give 3 to 4 per cent. extract; and we find 2·84 to 3·73 (p. 281). Rhine wine has from 1·0083 to 1·0097, specific gravity (p. 166), and should, therefore, contain 2 to 2·5 per cent. extract, and it yields from 1·33 to 2·15 (p. 281).

The specific gravity of Port wine varies from 1·0167 to 1·0227 (p. 166), and should therefore contain from 4 to 5·5 per cent. extract, and it gives from 3·75 to 5·24 (p. 282). We thus find everywhere lower estimates than those given by Balling, and yet we cannot impugn the experiments.

A still greater difference becomes apparent if we look more closely into the details of the various estimates. Thus, for example, we find the specific gravity of Madeira freed from alcohol 1·0170—1·0172—1·0170 (p. 165), and the corresponding extract per cent. 3·83—4·21—3·93 (p. 281). Further, sp. gr. 1·0179—1·0179—1·0179, the three being equal (p. 165), whilst in the extract we find 3·71—3·75—4·34 (p. 281).

The specific gravity of Teneriffe = 1·0152—1·0152—1·0152 (p. 165), and the extract 2·84—3·51—3·41 (p. 281); and the same in other cases. The agreement does not exist which is given by Liebig in his *Handw. I. s. 779* for beer, and by Balling in his “*Gährungs-chemie*” for beer and wine. The remarks appear to me of importance, inasmuch as this method has been adopted in making many estimates not only of wine extract, but also of the soluble constituents of wine must, estimates which may easily be found either too low or too high.

When must is examined closer agreement will be found, as it contains proportionably more sugar and less of other substances, whilst in wine there is either a great deal of sugar, and few salts or other matters, or just the reverse. The less sugar is present, the less possible is it to employ the saccharometric method (that is, to base the calculation upon the amount of sugar) in order to determine the quantity of tartaric and other acids, tartar and other salts, or, in one word, all such substances as appear in wine. If an error can occur amounting to  $\frac{1}{4}$  or  $\frac{1}{5}$  of the whole quantity, the method of analysis must be useless.

The case is different when the quantity of extract is large. We find, for instance, in *Lachryma Christi* 20·12 per cent. extract (p. 282). The sp. gr. of this wine freed from alcohol is 1·0805 (p. 167), which, according to Balling, gives 19·6 extract. *Muscat Rive-saltes* contains 24·5 per cent. extract (p. 282), whilst

this wine freed from alcohol is 1.0805 (p. 167), which, according to Balling, gives 19.6 extract. Muscat Rivesaltes contains 24.5 per cent. extract (p. 282), whilst the wine freed from alcohol is 1.0946 (p. 167), which, according to Balling, gives nearly 23 per cent. extract. We conclude, therefore, that Balling's estimates are too low for large, and too high for small quantities of extract.

## CHAPTER XXIII.

### INCOMBUSTIBLE CONSTITUENTS.

ALTHOUGH during the transformation of grape-juice into wine a large portion of the salts of organic as well as inorganic acids contained in it are precipitated, first with wine ferment, and afterwards with tartar, yet something of each remains dissolved. The crusting which occurs during winter is really separation of cream of tartar, which when once deposited in the form of crystals cannot be again dissolved, or at least but very imperfectly. Besides this, the presence of salts in wine is indicated by manifold reactions, of which we shall speak more particularly below.

If wine be evaporated, and what remains over burnt, a certain quantity of ash will be obtained; indeed this may be looked upon as one of the distinctive marks of genuine wine, as the amount of ash varies but little in wines of the same kind. I subjoin a table of the quantity of ash in some few kinds of wine, and remark at the same time that the difficulty which occurs in burning the ashes white, seems to indicate the presence of phosphoric acid in them.



The following amount of ashes was obtained by Messrs Gorkom, Viltman, and Moesman, from 100 C.C. wine (which is nearly equal to 100 grammes, 1543 grs.): the ashes are expressed in milligrammes (.015 grs.)

Madeira	No. 1	284	No. 5	177	No. 9	320	} average 255
	2	266	6	204	10	294	
	3	294	7	240	11	266	
	4	231	8	231	12	248	
Teneriffe	No. 1	311	No. 5	275	No. 9	329	} average 291
	2	320	6	311	10	266	
	3	275	7	302	11	302	
	4	354	8	294	12	257	
Rhine wine	No. 1	240	No. 5	168	No. 9	168	} average 193
	2	204	6	160	10	186	
	3	177	7	186	11	195	
	4	222	8	213			
Port wine	No. 1	240	No. 5	257	No. 9	231	} average 235
	2	240	6	266	10	222	
	3	231	7	195	11	213	
	4	257	8	231			
Bordeaux, ordinary	.	.	.	.	.	204	
„ Sauterne	.	.	.	.	.	186	
Hermitage	.	.	.	.	.	257	
Burgundy	.	.	.	.	.	204	
Lachryma Christi	.	.	.	.	.	488	
Muscat Rivesaltes	.	.	.	.	.	417	
Champagne	.	.	.	.	.	160	
Benicarlo	.	.	.	.	.	524	
Roussillon	.	.	.	.	.	604	
St. George	.	.	.	.	.	215	
Narbonne	.	.	.	.	.	417	
Tavella	.	.	.	.	.	231	
Langlade	.	.	.	.	.	204	
Cotes, white	.	.	.	.	.	204	
Bergerac	.	.	.	.	.	391	
Burgundy Pommard	.	.	.	.	.	204	

It will not be superfluous to subjoin here, what has been already stated respecting the inorganic constituents of wine.

And first, I may observe that every analysis has tended to prove that potash, soda, lime, magnesia, sulphuric, phosphoric, and silicic acid, and chlorine are contained in every wine, and iron in a good many. We have already spoken of alumina (p. 26).

Curiously enough, Fauré, Filhol and others have classed the organic constituents with the inorganic acids.

The largest amount of salts present in 1000 grammes of wine of the Gironde is, according to Fauré:

	In red wine.			In white wine.	
Bitartrate of potass . . .	0·66	1·97	..	0·91	1·43
Tartrate of lime . . .	0·06	0·24	..	0·06	0·13
Tartrate of alumina . . .	0·26	0·71	..	0·27	0·53
"    iron . . .	0·10	0·29	..	0·06	0·19
Chloride of sodium . . .	0·00	0·14	..	0·00	0·08
"    potassium . . .	0·00	0·10	..	0·00	0·06
Sulphate of potass . . .	0·11	0·26	..	0·10	0·25
Phosphate of alumina . . .	0·004	0·04	..	0·008	0·09

It is better at once to acknowledge that we can attain no certain results with respect to the grouping of such complex mixtures. Still greater uncertainty prevails as to grouping the constituents of the ash, which are otherwise of no importance, as far as a knowledge of wine is concerned.

The sum of all incombustible ingredients taken collectively, from which the carbonic acid produced

during the combustion of tartaric acid must be deducted, is as follows:—In 100 parts of Rhine it varies, according to Diez, between 0·28 and 0·11; that is, from  $\frac{1}{4}$ th to  $\frac{1}{10}$ th per cent. We get, therefore, as an average  $\frac{0\cdot28+0\cdot11}{2}=0\cdot19$ , agreeing exactly with the estimate given of eleven kinds of Rhine wine (p. 291). Champagne gives somewhat less, 0·16 per cent. Bordeaux Sauterne 0·19, equalling Rhine wine. Roussillon had the largest amount = 0·6 per cent. Benicarlo yielded 0·5 per cent. Both wines are rich in tartar, and must therefore leave a good deal of carbonate of potass in the ash.

The influence of the incombustible ingredients of wine has been spoken of already in several places. Most of them have no great effect upon the taste; potash is the most important, as it saturates a part of the tartaric acid, and remains in a state of solution. But tartrate and phosphate of lime, together with the small amount of common and other salts in the wine, have no great influence upon its flavour, colour or smell. As distinctive marks of the genuineness of the wines, they are of the greatest value. Let any one who wishes to convince himself whether a particular wine is adulterated or not, direct his attention to this point, and compare the ash with that of a genuine wine of the same kind as that under examination.

## CHAPTER XXIV.

### ODORIFEROUS CONSTITUENTS OF WINE.

A FEW years ago it seemed as if the cause of the multiplicity of agreeable odours diffused by wine would long remain enveloped in obscurity; but happily light has been shed upon this subject, and although we are still far from being able to say with certainty this or that kind of wine owes its peculiar character to such a substance, we have at least a satisfactory acquaintance with much that we wish to know. The attempt has often been made to separate the actual peculiar odoriferous ingredient out of aromatic wine. Since, however, we know that of the most important by weight of these odoriferous ingredients ~~both~~ only appears in wine, this plan may be given up, although Fauré tried to carry it out eight years ago, by distilling 500 grammes of wine, and out of 4 or 5 grammes of the first destillate kept as cool as possible, endeavouring to separate the odoriferous constituents. Even were a minimum of the ingredients which diffuse aroma to be thus obtained, this is not the most suitable manner for discriminating their nature.

The so-called fusel oils are those which have shed most light upon this subject, they being ethereal oils,

a mixture of several liquids in which the solid substances called fatty acids are dissolved: this mixture may be obtained either by distilling large quantities of wine (as in brandy distilleries), or by subjecting the grape-skins, which have already fermented with the juice, to distillation. In this manner substances actually existing in, and belonging to the wine, were obtained in such abundance as to allow of the mixed bodies being separated, and their individual constituents separately analysed. The result has shown that many of these ingredients may be artificially imitated; and those who adulterate wine have therefore attempted to improve the less aromatic wines by the addition of some odoriferous substance.

In treating shortly of these important bodies, I shall distinguish; 1st, those substances which are proper to all wines; 2nd, those which are developed in wine after a length of time; 3rd, such as depend entirely on the peculiarities of the places in which the grapes were grown.

I may here observe that this chapter differs in arrangement from the former part of this treatise.

I have taken into consideration substances whose existence, though not exactly proved, may yet be presumed in this or that kind of wine. For without giving a general view of the relations of these substances, I could hardly have spoken of the great variety and abundance of odoriferous ingredients which either have been or may be found in wine.

SUBSTANCES GENERALLY FOUND TO POSSESS A  
VINOUS SMELL.

It may appear singular, but is nevertheless true, that the ethereal ingredient which imparts to the grape-juice, after fermentation, the vinous odour (alcohol excepted) is itself fetid. No one can find it agreeable; it exactly resembles the liquid which imparts its peculiar odour to moutwyn.\*

After the œnanthic ether of wine had been examined by Liebig and Pélouze, I separated the same liquid from the fluid from which moutwyn is distilled,† and Pélouze has since permitted me to compare the liquids; and in combination, as in other qualities, when obtained by simple distillation, they resemble each other; in both cases the smell is disagreeable.

The substance is prepared not from the first portion of the destillate, but from that which comes over last, and in the case of moutwyn, from the residue after weak spirit has been distilled from the liquid. This remark is of some importance, inasmuch as it shows that œnanthic ether is not very volatile, which again renders it clear that the bouquet of aromatic wine cannot be ascribed to œnanthic ether. This

\* Moutwyn, literally "malt wine," is obtained by distilling the second *destillate*, and is also called in Holland "corn wine." We retain the designation "moutwyn."—Translator's note.

† Nat. en Scheik. Archief. deel. 5, p. 103.

ether is present in all wine. It is found in the preparation of brandy from wine, or in the first distillate, or in the fermented liquid, or in the moutwyn, at the end of the distillation, in quantities that can be collected; a certain quantity of the ether then will always distil over from brandy or moutwyn. According to this, it must exist in wine, and principally in that portion of the wine which has been freed from alcohol by distillation, and has acquired, as a watery fluid, a higher boiling point.

It may be distinguished by its smell alone. It is œnanthic ether, which diffuses a smell of fusel long after the disappearance of alcohol. That which remains after distillation, and has an unpleasant smell, cannot possibly impart an agreeable odour to the wine.

That smell which is peculiar to all wines must to a great extent be ascribed to œnanthic ether. It is clear that a volatile body appears together with œnanthic ether in wine, and imparts to it a smell differing from that of œnanthic ether. Œnanthic ether is found both in wine and in the liquid from which moutwyn is distilled; yet, though the mash smells most disagreeable, wine has no fetid smell. If however wine be distilled, the residue smells as disagreeably as the fermented mash.

The volatile substance existing in wine, which imparts to it, conjointly with œnanthic ether, its vinous aroma, is partly alcohol. If œnanthic ether be diluted with a good deal of weak spirit (as it is when it exists

in wine) an aroma is imparted to it, which, though not exactly that of wine, approaches it much more nearly than does that of simple ænanthic ether.

Brandy, that is, spirit out of wine, has not the smell of moutwyn, and this liquid, which contains an insignificant quantity of ænanthic ether, and is generally composed of water and alcohol, must therefore contain some other substance whereby the vinous smell is masked.

In moutwyn this substance is a peculiar volatile oil which does not appear in wine, and which I have called oleum siticum (corn oil). The peculiar smell of moutwyn is that of a mixture of weak spirit, ænanthic ether and corn oil. This corn oil is  $C^{24} H^{17} O$ .

I have dwelt more particularly upon these details, because all the books which treat upon this subject maintain that the vinous smell is derived from ænanthic ether, whereas I have already stated that the ether from wine which I obtained from Pélouze smelt like fusel oil from moutwyn. When diluted with water, it had not the slightest smell of wine.

We will now consider this substance more closely.



## CENANTHIC ETHER

exists in all wines, and imparts to them such a distinctive character, that if only a few drops of wine be left in a bottle, it will retain the vinous smell for days and weeks, not, however, having the agreeable odour of bouquet, but something like wine which has been exposed to evaporation. It is a fetid ethereal liquid, which, according to analyses made by Liebig and Pélouze, and confirmed by me, consists of  $C^{14} H^{13} O^2 + C^4 H^5 O$ ; according to Delffs, of  $C^{18} H^{17} O^3 + C^4 H^5 O$ ; that is, pelargonic ether. This point still remains undecided.

Cenanthic ether is found in the fusel oil of wine, moutwijn, and potatoe spirit, so that we are justified in considering it as a product of the fermentation of sugar. I do not, however, deny the statement made by Möhler, who obtained an oil by the distillation of quinces (*Pyrus Cydonia*) with water, which, when treated with potash, and after the potash compound had been decomposed by an acid, separated a fatty acid, which, so far as he could judge of it, coincided with cenanthic acid. It is very possible that this ether exists in quinces, but it does not exist in grape-skins. If, however, the fatty acid is all extracted from the grape-skins, how could wines prepared from grape-juice become possessed of cenanthic ether, which is never absent?

Œnanthic ether is prepared in large quantities by mixing the sediment of the wine with water, and then distilling it. A weak spirit is thus procured, which is re-distilled, and towards the end of the distillation the œnanthic ether is obtained.

As, however, the first raw spirit never yields more than  $\frac{1}{10000}$  of this ether, it has been calculated that not more than  $\frac{1}{40000}$  is contained in the wine. A large proportion of œnanthic acid is contained in the ether which is first obtained.

Œnanthic ether is procured in the same manner during the preparation of moutwijn. It flows at last from the first distillate, and can thus be collected. It is, therefore, not an ingredient of the grape, but a product of fermentation.

Before speaking more particularly of œnanthic ether, I will enumerate shortly

#### THE ODORIFEROUS SUBSTANCES DEVELOPED IN WINE IN THE COURSE OF TIME.

Besides the substances already named, the following may be reckoned among those which impart aroma to wine, which are originated in it by fermentation, and are either found, or may be presumed to exist in wine. They do not all exist in every wine, but one or several are found combined with œnanthic ether in aromatic wines. They are compounds of oxide of

ethyl, amyl, or propylene, with acetic, propionic, pelargonic, butyric, caproic, caprylic or capric acid.

I will mention each of these shortly and separately.

Acetic ether (acetate of oxide of ethyl).—This ether appears in most, perhaps in all aromatic wines, and is developed in them by time. The adulterators of wine are well acquainted with this fact, and know how to make use of it; acetic ether is regularly sold for this purpose, and added in proportionably small quantities to wines which are not aromatic, by which means their bouquet is very much improved. A very few drops are sufficient for a bottle of wine. Acetic ether may be prepared by distilling an acetic acid salt with alcohol and sulphuric acid; it is a volatile pleasant smelling liquid, a compound of  $C^4 H^3 O^3 + C^4 H^5 O$ . This ether always exists in freshly distilled brandy, and is found also in wine vinegar, which is thence so fragrant.

Butyric ether,  $C^8 H^7 O^3 + C^4 H^5 O$ .—If another acid be present, and butyric acid be mixed with alcohol, it may easily be resolved into butyric ether (ether butyricus). This is a thin volatile liquid, fragrant like pine-apple, though, like other aromatic substances, its fragrance is most evident when it is strongly diluted, in this case with alcohol. This ether is very much used by the English confectioners, who call it pine-apple oil.

Caprylic ether,  $C^{16} H^{15} O^3 + C^4 H^5 O$ ; a colourless fluid, with the fragrance of pine-apple.

Caproic ether,  $C^{12} H^{11} O^3 + C^4 H^5 O$ ; a very fragrant liquid, having the smell of melon and golden reinette. These last two ethers were found by Müller\* in the destillate of fermented juice of beet-root.

Pelargonic ether,  $C^{18} H^{17} O^3 + C^4 H^5 O$ ; an oily strong smelling liquid, which, according to Frankland, is found in remarkable quantities in Irish whisky.

Capric ether,  $C^{20} H^{19} O^3 + C^4 H^5 O$ ; a peculiar fragrant liquid, found by Rowney in the fusel oil of potatoes.

I may here notice acetate of capryl,  $C^4 H^3 O^3 + C^{20} H^{19} O$ ; a singularly fragrant liquid, whose existence may be presumed in some wines.

Propionic (metacetic) ether,  $C^6 H^5 O^3 + C^4 H^5 O$ ; was found by Winckler in Bergstrasse wine—the acid, at least, in the destillate of this wine. This ether is also very fragrant.

Butyl alcohol,  $C^8 H^{10} O^2$ , found by Wurtz † in the fusel oil of the beet-root, a volatile fluid, smelling like wine, which boils at  $109^\circ C. 228.2^\circ F.$

Hydrated oxide of amyl (amylic alcohol),  $C^{10} H^{11} O + H O$ . This liquid, which behaves like a true alcohol, is commonly called potatoe fusel oil: it appears as a product of the fermentation of sugar, and has nothing in common with potatoe starch. It is sometimes found in moutwijn, and has been detected in the fermented juice of beet-root. Its presence may be assumed in

\* Journal de Pharm. Série 3, tom. xxii. p. 160.

† Ann. der Ch. und Pharm. Bd. 85, s. 197; Bd. 93, s. 107.

many kinds of wines, either free or combined with acids, so that the oxide,  $C^{10} H^{11} O$ , combines with acetic or with caprylic, caproic, capric, butyric, pelargonic, propionic, or any other acids, as does oxide of ethyl in salts of oxide of ethyl. Chancel found that in wine-fusel oil prepared from grape-skins more than half consisted of hydrated oxide of amyl; and Faget\* has detected in the more sparingly volatile ingredients of this liquid, a colourless pleasantly aromatic fluid, insoluble in water, and known as caproyl alcohol,  $C^{12} H^{14} O$ .†

Hydrated oxide of amyl has as disagreeable an odour as cœnanthic ether, but some of the compounds are very fragrant.

Hofmann first remarked that a liquid was sold in England under the name of grape or cognac-oil, and used to give the smell of cognac to inferior kinds of spirit; and we may expect this substance to appear in French wines. He had not enough of it to ascertain accurately its chemical composition, but found oxide of amyl in it.

Oxide of amyl forms plenty of fragrant combinations. They appear in old cellared wines, whilst hydrated oxide of amyl must be sought in younger wines.

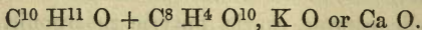
Since Breunlin ‡ has made us acquainted with amylo-

\* Comptes Rendus, tom. xxxvii. p. 730, in Ann. der Ch. u. Pharm. Bd. 88, s. 325.

† Ann. der Ch. u. Pharm. Bd. 81, s. 90.

‡ Ibid. Bd. 91, s. 314.

tartaric acid, we may expect to find not only this, but also amylo-tartrate of potash and of lime,



Balard\* has taught us that hydrated oxide of amyl must appear in many wines. He obtained it from the residue of wine mixed with œnanthic ether after distilling brandy. He also first drew attention to the compound of oxide of amyl with tartaric acid.

Amylo-malic acid, described by Breunlin, is like amylo-tartaric acid fixed, and may therefore appear in wines containing these acids.

Acetate of amyl,  $C^4 H^3 O^3 + C^{10} H^{11} O$ .—A liquid having the same odour as acetic ether.

I may pass over almost in silence butyric acid, caproic, caprylic and capric, pelargonic and propionic oxide of amyl, since to a very great extent they agree with compounds of these acids with oxide of ethyl. We have already mentioned the tartaric acid compound, which is a syrup-like liquid, having a bitter taste, and acid reaction.

Hydrated oxide of propyl.—Chancel has discovered in the fusel oil of wine a propyl alcohol, the composition of which is  $C^6 H^7 O, HO$ . More than half of the eighteen litres of fusel oil which were expended on this experiment were hydrated oxide of amyl; in the other half Chancel discovered aldehyde, hydrated oxide of butyl, and propylene, which make up the most volatile portions of the first distillate.

\* An. de Ch. et de Phys. Série 3, tom. xii. p. 294.

Hydrated oxide of propylene boils at  $96^{\circ}5$  C.,  $206^{\circ}$  F., has by no means an unpleasant vinous odour, and is insoluble in water.

Butyrate of propyl,  $C^8 H^7 O^3 + C^6 H^7 O$ .—This compound, which possesses the purest pine-apple smell, was obtained by Chancel by means of butyric and muriatic acid, and hydrated oxide of propylene.

Aldehyde.—I remarked before that Chancel found aldehyde in fusel oil, and it may therefore be found in wine. Labens\* has also announced its presence in wine. Aldehyde in a diluted state ( $C^4 H^4 O^2$ ) is a pleasant smelling liquid. But if it be found in wine, but a very small quantity can exist in it; and then also Acetal,  $C^4 H^3 O + C^4 H^5 O + H O$ , must be present. This is a hydrated oxide of acetyl and oxide of ethyl, an ethereal liquid of very pleasant odour. Acetal appears to be principally found in Hungarian wines, many of which have the characteristic smell of acetal dissolved in diluted alcohol. This substance is soluble in alcohol, and also in water.

Besides these, compounds of oxide of ethyl with tartaric, racemic, and malic acid appear in wine according as the acids are found, but some of them are scentless, and others have no agreeable smell. At any rate they give some flavour to the wine, and as they are constituents of wine they must not be passed over in silence. I will describe them shortly.

Tartaric ether and water, etherised tartaric acid,

\* Journ. de Pharmacie, Janv. 1855, p. 37.

$C^8 H^4 O^{10} + C^4 H^5 O$ , HO, is formed at an ordinary temperature, if tartaric acid be brought into contact with alcohol.

This is the case in wine, and this acid combined with oxide of ethyl will therefore be found in all wines. It crystallises in rhombs, is destitute of smell, and has a sweet sour taste; if it be produced from free acid in wine, the wine must become sweeter.

Distillation with water converts it into alcohol and tartaric acid. We have, therefore, no means of detecting its presence in wine, though we feel convinced that it does exist.

Racemic ether and water,  $C^8 H^4 O^{10} + C^4 H^5 O$ ,  $^2HO$ .—This substance is distinguished from the preceding by containing one more equivalent of water. In other respects it entirely corresponds to it; it will be found in wines containing racemic acid, although its presence also cannot be proved.

Citric ether,  $C^4 H^2 O^4 + C^4 H^5 O$ .—This is a yellowish oily liquid, which, having itself the smell of sweet oil, cannot certainly impart fragrance to the wine. The presence of this ether compound in wine cannot be proved, as distillation with water resolves it into alcohol and citric acid. It would make Burgundy wine bitter. (Compare p. 130.)

Malic ether,  $C^4 H^2 O^4 + C^4 H^5 O$ , coincides in most points with citric ether, and is equally decomposed by distillation.

Fumaric ether,  $C^4 HO^3 + C^4 H^5 O$ .—This ether



compound has an oily consistence, and a pleasant fruity smell. If we have no right to assume that it is present in wine, we are at least certain that wines containing malic ether will furnish fumaric ether to the alcohol distilled from them.

Margaric ether,  $C^{34} H^{33} O^3 + C^4 H^5 O$ .—Rowney found margaric acid in fusel oil, and we may therefore presume that margaric ether will exist in wine. But this substance is a solid colourless substance and can add nothing either to the smell or taste of the wine.\* Margaric acid was found by Glassford in the fusel oil of Scotch whiskey, and by Kolbe in moutwyn.

These are the substances whose presence in wine may be assumed, or which have been obtained either from the wine itself, or from the products of distillation. Time will perhaps discover more, but the odiferous substances already mentioned are sufficient to account for the immense variety of bouquet; since one, and now another, aromatic substance is found in wine, and sometimes two, three, or even more in different variable proportions.

How now are the above-named substances formed in wine?

In order to understand this clearly, we must first study the formation of ether, a compound of oxide of ethyl with an acid, it is indifferent what kind of ether is produced, if it be readily decomposed by the action of other acids.

\* Liebig's Ann. Bd. 54, s. 104; Bd. 41, s. 53 (Kolbe).

It is well known that such chemical operations as are speedily brought about by means of heat, or other agents, may be effected more slowly without such assistance. Liebig\* dissolved oxalic acid in alcohol by heat till it was saturated, and left it standing at a temperature of from  $40^{\circ}$  to  $50^{\circ}$  ( $104^{\circ}$  to  $122^{\circ}$  F.) After it had stood for some months he found oxalic ether and oxalo-vinic acid in it.

Hippuric acid forms hippuric ether in the same manner. But benzoic acid requires a much longer time before any ether is formed from it.

Tartaric acid has the power of forming rapidly, when in contact with alcohol, without the assistance of heat or any other body, etherised tartaric acid.

This is the first point we have to consider, in order to obtain a clear idea of the origin of the substances existing in wine. Free tartaric acid is contained in grape-juice. As soon, therefore, as alcohol is formed out of sugar, etherised tartaric acid will also be produced, and remain dissolved in the wine. This body is destitute of odour, and cannot, therefore, impart any fragrance to the wine. Its taste, however, being much less sharp than tartaric acid, may render the wine sweeter, without causing any actual increase of sugar, which indeed can hardly be assumed after the wine has been bottled (p. 113). Etherised tartaric acid is easily decomposed, and when the watery solution is kept it resolves itself again into tartaric acid and alcohol.

\* Ann. der Ch. u. Pharmacie.

On this account every acid produced from wine, either during fermentation or at a later period in any other manner, may, by separation of the tartaric acid, originate the ether of the new acid; and the tartaric acid thus thrown off may serve for the reproduction of etherised tartaric acid, and thus the whole process begins again. Just as the decomposition of one sulphovinate may give rise to another sulphovinate, so may the ether, freed from tartaric acid, combine with another acid.

During the fermentation of grape-juice, a very rapid formation of etherised tartaric acid may be expected. This occurs during the first days of fermentation, before the liquor has acquired any vinous odour.

A second period now begins, which we have distinguished by the name of after-fermentation (p. 91). During this period the peculiar vinous smell of the liquid is developed, and as this must be attributed to œnanthic ether, we have now to seek after the origin of œnanthic acid. If the œnanthic acid exist in the wine (and it is partly contained in it in a free state, for it can be so obtained by distilling the sediment) it will decompose the scentless etherised tartaric acid, and give rise to œnanthic ether, that is, to the liquid which imparts vinous odour to all wines.

The formation of œnanthic ether in wine is preceded by the production of many fatty acids, most of which are formed in the course of time, and impart a peculiar kind of fragrance to old wines.

How now is œnanthic acid produced in wines in process of formation?

The existence of this acid, not only in the fusel oil of wine but also in that of moutwyn and potato spirit, dissipates every idea of its being present in grape-juice. But it is possible that this acid is formed from a fat existing in the juice, skins, or stones of the grape, and also in potato flour and moutwyn. This is the more probable, as margaric acid,  $C_{34}H_{34}O_4$ , exists in all fusel oil, even in that of wine. It is known that sugar gives rise to fats. Wax is partially formed from grape sugar (honey); animals which get nothing but starch without fat, starch which passes into sugar, are thus furnished with fat, as was proved by infallible experiments a few years ago. Avequin found a kind of wax (cerosine) on the sugar-cane, when there was much fat, there was proportionably less sugar. The white wax upon purple grapes and plums is fat, and it is formed from sugar of the fruit.

The origin of œnanthic acid might be accounted for by either of these causes, but which is the real one? This is a question which cannot be immediately answered. Fat exists in the grape-juice, and more especially in the stones (p. 44). Much fat is not required to originate the odoriferous substances found in wine, and the fat of the grape stones is more than sufficient to furnish the fatty acids necessary for the ethyl and methyl compound in wine. There is

even more than enough, since fat is found in the sediment of the wine (p. 240).

If we remember that in animal bodies compounds of fatty acids containing 8, 12, 16, and 20 times  $\text{CH} + \text{O}^4$ , with glyceryl oxide (glycerine), are formed out of margarin; from butter, butyrin, capron, capryl, and caprin, we must first devote our time to the fatty substances of gr ape skins and juice; since it is absurd to search for a fat as the product of fermentation, if fat be known to exist in the fermenting substances.

Now, whether the fat of wine proceed from the stones, from the juice itself, or from the skins, it takes part in the fermentation, and may as easily undergo alteration here as elsewhere. If the oil of the grape stones contain margarin, this may, during fermentation, yield as butter does butyrin, capron, &c., and be the primary source of the many fatty acids, faint traces of whose presence are found in wine.

The difficulty here is, whether margaric acid, considered by Heintz as a mixture of palmetic,  $\text{C}^{32} \text{H}^{32} \text{O}^4$ , and stearic acid,  $\text{C}^{36} \text{H}^{36} \text{O}^4$ , could by absorbing oxygen alone form butyric, caproic, caprylic and capric acids, which contain 8, 12, 16, and 20 times  $\text{CH} + \text{O}^4$ . But as very little fatty acid exists in wine (p. 240), an excess of oxygen would be always present in the air held in solution in the wine.

The same oxidation would take place by the resolution of margaric into  enanthic acid, whether it be considered

to be  $C^{14} H^{14} O^3$ , or as Delffs\* writes,  $C^{18} H^{18} O^4$ , that is pelargonic acid. I can here state nothing positively, since the transformation of margaric into ceanthic or butyric acid, &c., during fermentation, has never yet been ascertained. An examination of this subject appears to me of importance. Fatty substances are easily resolved into one another, and in wine this cannot be otherwise.

Another explanation of the origin of fatty acids in wine, may be found in the supposition that they are products of the fermentation of sugar or other fermenting substances, or perhaps of one of the components of ferment itself. An observation of Scharling's,† which concerns the production of butyric acid, may be mentioned in connexion with the formation of fatty acids. Grated potatoes (that is, potato cellulose), freed by water from all starch, yield butyric acid in three days, at a temperature of from  $30^{\circ}$  to  $35^{\circ}$  ( $86^{\circ}$  to  $95^{\circ}$  F.) Carbonic acid is at the same time developed.

If in such a case it is really the cellulose which ferments, and not the fat of the cellulose which is resolved into butyric acid, then attention should be paid to this matter in every case in which the pulp or skin is allowed to ferment in wine; since both of these bodies are principally formed of cellulose.

But Pélouze and Gélis‡ saw butyric acid formed

\* Ann. der Ch. u. Pharm. Bd. 80, s. 290.

† Ann. der Ch. u. Pharm. Bd. 49, s. 313.

‡ Ann. de Ch. et de Ph. tom. x. p. 434.

from dextrin as well as from different kinds of sugar, when these substances were mixed with caseine and vegetable gluten in water and chalk, and allowed to ferment. The gluten behaves just like caseine.

The formation of butyric acid developed carbonic acid, and hydrogen gas, at first only from 10 to 15 per cent. of the total amount of gas was hydrogen, but afterwards equal volumes of each.

They afterwards found, what is of great importance for our purpose, alcohol among the products of this fermentation.

If the production of a copious amount of butyric acid does not check the simultaneous formation of alcohol, then it is certain that during the formation of wine (even before much alcohol was formed), the conditions necessary to the production of a fatty acid from the sugar of grapes might exist.

The change of sugar into butyric acid is generally thus represented:—

1 equiv. sugar	. . . . .	$C^{12} H^{12} O^{12}$
1 butyric acid	. . . . .	$C^8 H^8 O^4$
4 carbonic acid	. . . . .	$C^4 O^8$
4 hydrogen gas	. . . . .	$H^4$

Such a resolution of sugar, or what is the same thing here, of the cellulose of grape-pulp in wine, is improbable. But the development of hydrogen gas during the butyric acid fermentation is sometimes quite imperceptible, and sometimes does not occur.

It has the same effect upon the reaction if oxygen

be added, which removes the hydrogen as it becomes free and combines with it.

Butyric acid is not, however, the fatty acid first formed in wine; it is usually originated at a later period, and forms one of the odoriferous ingredients of old wine; and hence in turning our attention to butyric acid, I have considered it not as a primary but as a secondary substance in wine. The well-ascertained fact must, however, be stated that butyric acid is formed out of cellulose and sugar, thereby establishing that the fatty acids of wine are not necessarily derived from the fatty substances of the stones and skins or of the grape-juice, but may come from a source which depends entirely on the decomposition of the sugar.

The first fatty acid found with oxide of ethyl immediately after its formation in wine, is œnanthic acid. Since œnanthic acid appears to be the source of the butyric, caproic, and other acids formed at a later period, we must devote some attention to it. It has been asserted that œnanthic acid cannot be a product of fermentation, because none is obtained if ferment be added to sugar to induce fermentation. The real state of the case is this: during fermentation, under the influence of the ferment which is undergoing change, no œnanthic acid is obtained; but this does not prove that this acid is not produced when ferment is forming. I consider this point of sufficient importance to merit special consideration.

When potato syrup is fermented (to make spirit),



only a very small portion of ferment can be formed, since but little malt is added. Much hydrated oxide of amyl is originated, and but little œnanthic ether.

An energetic formation of yeast takes place during the preparation of wine and moutwyn, and at a later period a like decomposition. In both cases much œnanthic ether is formed.

If we consider that sugar and water mixed with ready-formed ferment yields no œnanthic ether, we must connect fermentation with formation of ferment and of œnanthic ether, but not with the decomposition of ferment.

We know that ferment, the contents of the cells at least, is composed of albumen and cellulose, which is here indifferent. A substance is found in the ferment cells which can be extracted with water, and is no longer what it originally was—albumen. It is a substance the oxygenous contents of which bear the same proportion to the mother substance (albumen) as 3 to 2, that is, it contains  $\frac{1}{3}$  more oxygen than does albumen.\* On this account the formation of ferment is promoted by air (p. 55), but whilst the ferment is forming it may easily withdraw oxygen from the sugar and produce œnanthic acid, that is, supposing no excess of air to be present.

This subject deserves and may easily be subjected to a closer investigation. Sugar dissolved in water ferments if brought into contact with vegetable gluten

\* Scheik. Onderz. d. 2, p. 456; and p. 261 of this work.

and dextrin, and out of this mixture ferment can be formed. And if under these circumstances œnanthic acid be formed, it would be because oxygen had been withdrawn from the sugar by the formation of that ferment matter from vegetable gluten, which is soluble in water and richer in oxygen than vegetable gluten.

If œnanthic acid be  $C^{14} H^{14} O^3$ , then we should have for example—

2 equiv. sugar . . . . .	$C^{24} H^{24} O^{24}$
œnanthic acid . . . . .	$C^{14} H^{14} O^3$
Alcohol . . . . .	$C^4 H^6 O^2$
Carbonic acid . . . . .	$C^6 O^{12}$
Water . . . . .	$H^4 O^4$
Oxygen abstracted for the forma- tion of ferment . . . . .	$O^3$

If œnanthic acid be pelargonic acid,  $C^{18} H^{18} O^4$ , then we have

Sugar . . . . .	$C^{24} H^{24} O^{24}$
Pelargonic acid. . . . .	$C^{18} H^{18} O^4$
Alcohol . . . . .	$C^4 H^6 O^2$
Carbonic acid . . . . .	$C^2 O^4$
Oxygen abstracted for formation of ferment. . . . .	$O^{14}$

I have given the two formulæ on account of the doubtful composition of the œnanthic acid. Whoever wishes to test this formation must let sugar ferment with yeast, air being excluded, otherwise the air furnishes the oxygen which is necessary to decompose the ferment.

Soon after the formation of œnanthic acid in wine, the peculiar vinous smell is developed, that is, œnanthic

ether is originated, doubtless by the decomposition of existing etherised tartaric acid, since œnanthic acid, which is fatty and not very acid, is certainly incapable of separating a portion of oxide of ethyl out of alcohol.

We might here conclude our considerations upon the origin of the odoriferous constituents, if our only object were to pursue the subject to the point reached by the present state of science, which ascribes vinous odour to œnanthic ether.

But time developes aroma, varying, in different wines, in proportion to the amount of the above-named substances formed in them.

We most commonly find acetic ether in aromatic old wines. The oxygen of the air dissolved in wine, and existing in the bottles, changes alcohol,  $C^4 H^6 O^2$ , first into aldehyde,  $C^4 H^4 O^2$ , (which may exist together in wine,) and thus, by progressive oxidation of this aldehyde in  $C^4 H^3 O^3$ ,  $H O$ , that is, into acetic ether, which is hence found in all wine. It can decompose œnanthic ether, separate œnanthic acid, and form acetic ether.

In this manner the formation of the acetic ether, which is always found in old cellared wines, is explained; perhaps the acetic acid, assisted by the tartaric acid, etherises a portion of the alcohol. It is well known that acetic ether is formed, after a time, in absolute alcohol, in which it did not previously exist. But the alcohol we are treating of here is not absolute, as it is diluted in wine. A decomposition

of œnanthic ether by means of the œnanthic acid in wine seems to me, however, not improbable, as in proportion to the formation of acetic and compound ether (of which we have still to treat) in old wine will be the diminution of œnanthic ether. The aroma increases, and the disagreeable odour decreases.

The formation of acetic acid and acetic ether in wine may, however, be very different.

Among the volatile substances which may exist in wine is one which, on several accounts, deserves to be mentioned here. It is Nöllner's aceto-butyric acid, which has been examined in detail by Nickles.\*

Nöllner prepared this acid from raw tartar, which he boiled with water and hydrated lime, decomposing the neutral tartrate of potash with gypsum, in order to procure tartrate of lime. After filtering the liquid, he mixed the tartrate of lime which had been obtained (and which contained the organic matter of wine ferment) with water, and placed it in the sun.† Carbonic acid and a soluble lime-salt were developed, out of which by sulphuric acid a volatile acid was separated, which quickly resolved itself into butyric and acetic acid, but according to Nickles, should be called a peculiar compound of both acids =  $C^6 H^5 O^3, HO$ , a compound like that of the metacetic acid, but with quite different properties.

The examination instituted by Nickles renders it

\* Liebig's Ann. Bd. 61, s. 343.

† Berzelius, Lehrbuch der Chemie, 5 Aufl. Bd. 4, s. 256.

sufficiently clear that this is a peculiar monobasic acid, according to the ordinary, not the double formula, which nevertheless fully expresses the compound,  $2 (C^6 H^6 O^4) = C^4 H^4 O^4 + C^8 H^8 O^4$ ; that is, hydrated acetic and butyric acid.

This acid is formed out of tartaric acid. Acetic and butyric ether appear in cellared wine; they may, as we see, be formed in combination from the decomposition of tartaric acid. If this be the case, then tartaric acid is thereby decomposed, the wine becomes less acid, and this is observed to occur as the wine ages. (Compare p. 111.)

Butyric and acetic ether are odoriferous components of wine. If aceto-butyric acid forms a compound ether, it also must be sought among the constituents of wine.

It is known that tartaric and citric acid, without lime, and dissolved in water in a pure state, contain, after a time, a large amount of acetic acid. The decomposition of tartaric acid in wine can no longer be doubted.

There is, therefore, a real connexion between the gradual sweetening and increase of aroma in wine, which occurs in the course of time.

When we now bring this to bear upon what we have already said respecting the facility with which etherised tartaric acid is formed, then we perceive that butyric and acetic ether may be produced by the change of the tartaric acid in wine into butyric and acetic acid.

Acetic and butyric ether may be formed, therefore, independent of œnanthic ether, and this may serve to be resolved, in course of time, into other ethers of the fatty acids.

Here we must make a distinction. When œnanthic ether is resolved into another fatty acid, more oxide of ethyl is necessary to saturate this acid if the fatty acid which is hereby originated has a lower atomic weight, and less if it possess a greater atomic weight. Less, therefore, if, for example, capric acid ( $C^{20} H^{20} O^4$ ), more if caproic acid ( $C^{12} H^{12} O^4$ ), or butyric acid ( $C^8 H^8 O^4$ ), are formed out of œnanthic acid ( $C^{14} H^{14} O^3$ ), or pelargonic acid ( $C^{18} H^{18} O^4$ ).

Some tartaric acid always, however, remains in wine, and by its power of etherising, it strengthens every acid that forms in wine. The formation of oxide of ethyl in wine presents no difficulty.

The question is, how do the fatty acids arise from œnanthic or pelargonic acid ?

We will give a sketch of both.

Let œnanthic acid be =	. . .	$C^{14} H^{14} O^3$
4 equiv. œnanthic acid	. . .	$C^{56} H^{56} O^{12}$
2 capric acid	. . . .	$C^{40} H^{40} O^8$
1 caprylic acid	. . . .	$C^{16} H^{16} O^4$
If œnanthic acid be pelargonic acid		$C^{18} H^{18} O^4$
2 equiv. pelargonic acid	. . .	$C^{36} H^{36} O^8$
1 capric acid	. . . .	$C^{20} H^{20} O^4$
1 caprylic acid	. . . .	$C^{16} H^{16} O^4$
or 6 pelargonic acid	. . . .	$C^{108} H^{108} O^{24}$
5 capric acid	. . . .	$C^{100} H^{100} O^{20}$
1 butyric acid	. . . .	$C^8 H^8 O^4$

And many other formulæ might be given. The resolution of the homologous fats is easily effected artificially.

The difficulty is not in explaining the changes they undergo, but in the experimental proof as to the origin of the œnanthic ether.

This, as we have already mentioned, undergoes a peculiar change in wine, and the newly-formed acid remains combined with oxide of ethyl. As butyric, caprylic, caproic, and capric ether are formed in wine, œnanthic ether, which is the origin of all, diminishes.

The formation of oxide of capryl,  $C^{20} H^{19} O$ , HO, in wine needs as little explanation as does that of propionic acid,  $C^6 H^5 O^3$ , HO. Of the latter it may be said, that it holds a middle position between acetic acid  $C^4 H^4 O^4$ , and butyric acid  $C^8 H^8 O^4$ .

I now turn to the consideration of the manner in which hydrated oxide of amyl,  $C^{10} H^{11} O + HO$ , is produced: this liquid composes the greater part of potato fusel oil, and also appears in wine. That this body is a product of the fermentation of sugar is an ascertained fact, and we may represent it thus—

5 equiv. sugar	. . . . .	$C^{60} H^{60} O^{60}$
4 „ hydrated oxide of amyl.	. . . . .	$C^{40} H^{48} O^8$
20 „ carbonic acid	. . . . .	$C^{20} O^{40}$
12 „ water	. . . . .	$H^{12} O^{12}$

This hydrated oxide of amyl deserves to be mentioned as much as the œnanthic ether in wine, since it forms quickly, and combines, like it, with butyric

and caproic acid, and with acetic acid, &c., water being separated, and compounds of butyric, caproic, and acetic oxide of amyl are formed, which, to a certain amount, are found in wine.

Most of these salts of oxide of amyl are odoriferous liquids. We mentioned acetic amyl ether (p. 303), but many others appear in different wines.

Hydrated oxide of amyl may also be formed from alcohol.

5 equiv. alcohol . . . . .	$C^{20} H^{30} O^{10}$
2 „ hydrated oxide of amyl . . . . .	$C^{20} H^{24} O^4$
6 „ water . . . . .	$H^6 O^6$

I must observe here that the compounds of oxide of amyl in wine never preponderate over the compounds of ethyl; that in wines containing free tartaric acid, amyl compounds appear in but small proportion, while alkaline and neutral solutions give rise to hydrated oxide of amyl, and its formation is stopped by the addition of tartaric acid to fluids in which it would otherwise be produced in great abundance.

The following formulæ deserve notice. Hydrated oxide of ethyl, of propylene, of butyl, and of amyl, may be formed thus—

2 equiv. sugar . . . . .	$C^{24} H^{24} O^{24}$
Hydrated oxide of amyl . . . . .	$C^{10} H^{12} O^2$
„ „ of propylene . . . . .	$C^6 H^8 O^8$
Carbonic acid . . . . .	$C^8 O^{16}$
Water . . . . .	$H^4 O^4$



2 equiv. sugar . . . . .	$C^{24} H^{24} O^{24}$
Alcohol . . . . .	$C^4 H^6 O^2$
2 equiv. hydrated oxide of propylene	$C^{12} H^{16} O^4$
Carbonic acid . . . . .	$C^8 O^{16}$
Water . . . . .	$H^2 O^2$
2 equiv. sugar . . . . .	$C^{24} H^{24} O^{24}$
2 „ hydrated oxide of butyl . . . . .	$C^{16} H^{20} O^4$
Carbonic acid . . . . .	$C^8 O^{16}$
Water . . . . .	$H^4 O^4$

Lastly, I must draw attention to an observation made by Eichhorn,\* who analysed the fat of potatoes. His opinion, which deserves consideration, is that oxide of amyl occasionally gives rise to the fatty acids in fusel oils, and therefore in wine. Thus, for example, oxide of amyl is  $C^{10} H^{11} O$ , anhydrous acetic acid  $C^4 H^3 O^3$ . Together they are  $C^{14} H^{14} O^4$ , that is, œnanthylic acid =  $C^{14} H^{13} O^3 + HO$ .

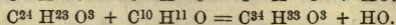
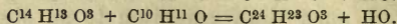
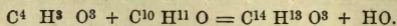
If this œnanthylic acid combines with oxide of amyl,  $C_{10} H_{11} O$ , laurostearic acid is formed,  $C_{24} H_{24} O_4 = C_{24} H_{24} O_3 + HO$ . If this last acid combines with oxide of amyl, margaric acid,  $C_{34} H_{34} O_4$ , is again produced.

According to Eichhorn the fatty acid compounds of oxide of amyl, pass in course of time into a new fatty acid, and usually in the following manner:—

1 equiv. acet. oxide of amyl	$C^{14} H^{14} O^4$	= 1 equiv. œnanthylic acid.
1 „ butyr. „	$C^{18} H^{18} O^4$	= 1 „ pelargonic acid.
1 „ œnanth. „	$C^{24} H^{24} O^4$	= 1 „ laurinic acid.
1 „ caprinic „	$C^{30} H^{30} O^4$	= 1 „ solanostearic acid.
1 „ laurinic „	$C^{34} H^{34} O^4$	= 1 „ margaric acid.

\* Pogg, Ann. Bd. 87, s. 227.

These observations merit future consideration. If metameric substances be converted into one another in the course of time, then, supposing a sufficient quantity of oxide of amyl to be present, acetic acid would eventually become margaric acid, for acetic acid and oxide of amyl are—



Delffs\* gives the following summary respecting the formation of so-called alcohols,  $C^n H^{n+2} + O^2$ ; all are considered to arise from  $C^{24} H^{24} O^{24}$ , that is, 2 equiv. anhydrous grape sugar.

Propyl alcohol and alcohol.....  $2 C^6 H^8 O^2 + C^4 H^6 O^2 + 8 C O_2 + 2 H O.$

Butyl alcohol .....  $2 C^8 H^{10} O^2 + 8 C O_2 + 4 H O.$

Propyl alcohol and amyl alcohol..  $C^6 H^8 O^2 + C^{10} H^{12} O^2 + 8 C O_2 + 4 H O.$

Capronic alcohol and alcohol.....  $C^{12} H^{14} O^2 + C^4 H^6 O^2 + 8 C O_2 + 4 H O.$

Lastly, I must mention that as a rule the most odoriferous ingredients predominate in wines containing free acids—tartaric acid, for example. Very sweet wines obtained from grapes which contain either very little free acid, or have this acid softened by excess of sugar, are, in general, much less fragrant than some French or Rhenish wines. This confirms the opinion I have given as to the influence of the free tartaric acid in the formation of the compound ethers.

The following experiments deserve notice. If grape juice be filtered through animal charcoal, and the

\* Lehrb. der Org. Chemie, 1855. s. 351.

liquid then allowed to ferment, a scentless wine is obtained.

If grape juice be evaporated, the residue mixed again with water, and allowed to ferment, a wine without aroma is obtained.

If grape juice be mixed with olive oil, and the juice fermented after the oil is separated from it, a wine without bouquet is again obtained.\*

There are vegetables which contain sugar and ferment, but during fermentation yield no alcohol, as, for example, onions. If they do furnish alcohol, the amount is not in proportion to the quantity of sugar contained in them. Braconnot† first examined this subject, and found mannite, vegetable mucus, and lactic acid among the products of fermentation. Kirchner found that the composition of the mucilaginous substances discovered by Braconnot and of gum was the same; and Pélouze, Jules Gay-Lussac, and others, have examined these products in detail. Pélouze found that hydrogen gas was evolved during the fermentation of these vegetables, but it is often wanting, and does not appear to belong necessarily to this fermentation, which is called mucous fermentation, because the formation of vegetable mucus generally renders the liquid thick (p. 127).

The mannite which is thus formed from sugar is  $C^6 H^7 O^6$ , the lactic acid and the gum have the com-

\* Schubert. *Techn. Chemie*, Erlangen, 1854, s. 352.

† *Ann. de Chemie*, tom. lxxxvi. p. 97.

position of sugar. Sugar therefore forms mannite, lactic acid, and vegetable mucus; and if, as is often the case when the temperature of the fermenting liquid is kept between  $30^{\circ}$  and  $40^{\circ}$ , ( $86^{\circ}$  and  $104^{\circ}$  F.,) no hydrogen be evolved, this gives rise to non-hydrogenous products, and accounts, according to Schmidt,\* for the production of succinic acid, which he found in all liquids fermented in this manner.

As the opinion that in all the different periods of fermentation the sugar of grape juice undergoes only one transformation, viz. that into alcohol and carbonic acid, has been found utterly erroneous, we may expect, in future, that the careful analysis of large quantities of wine will discover new varieties of substances in different kinds of wine.

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#### ODORIFEROUS SUBSTANCES WHICH DEPEND ON THE PLACES WHERE THE GRAPES ARE GROWN.

Under this head, I understand, besides those substances in wine which determine the nature of the odoriferous ingredients already treated of, more particularly ethereal oils, which exist in abundance in the vegetable kingdom, and appear in all parts of vegetables, and even in fruits. We perceive in the juice of single grapes, muscadels, for instance, aroma com-

\* Handwörterbuch, v. Pogg, Bd. 3, s. 124.

bined with agreeable flavour. It is, therefore, no wonder that wine prepared from such grapes should retain the aroma of the juice. This bouquet is, therefore, not the effect of fermentation, nor the product of a substance first originated during fermentation, for it existed previously in the juice. We are now treating only of such pre-existent substances. As a rule they are seldom found in the grapes of our colder districts. The aroma which the wines produced from such grapes possess, is a product of fermentation and not a pre-existent substance. But fragrant oils are mostly met with in the grapes of warmer districts. And, indeed, the larger proportion of the volatile oils, which fill so important a place in organic chemistry, are to be found in plants belonging to warmer climates. They abound in flowers and in fruits, pine apples and our reinettes and peaches are well provided with them.

The amount of volatile oil existing in grapes and imparting aroma to wine, is so insignificant that it will probably be a long time before we are thoroughly or accurately informed concerning them. How should they be separated or examined?

There is one other means of discriminating these substances, which has already been used scientifically, and that is the identity of aroma in such liquids when prepared in large quantities. This method is, however, by no means satisfactory, for resemblance in odour does not justify us chemically in concluding

that there is no difference in kind. But we know that science is greatly indebted to this method, and may fearlessly make use of it here.

What kinds of ethereal oils are employed to increase the bouquet of different wines?

Portions of fragrant plants are mixed with the must in order to extract their ethereal oil.

As these plants can be independently examined, we learn from them the quality of those volatile substances which exist in grapes in such small quantities that it is necessary to increase them artificially. Different plants are resorted to for different wines, and we have rose leaves, lime and elder flowers, the leaves of the *spiræa ulmaria* (meadow sweet), the peel of quince pears, the blossom of wild vines, leaves of *salvia setacea* (sage or clary), and perhaps the ferment oil of the centaury. These and others are commonly added to improve the aroma of wine. Probably the odoriferous ingredients actually exist in the juice of some of the grapes. In order to give the bouquet of good Bordeaux to less agreeable wines, it has become customary to put violet roots and the roots of the Florentine iris in other wine. They contain an agreeably-scented stearopten, which Dumas found to be  $=C^4 H^8 O^1$ .

Bley\* has separated a fragrant ethereal oil by distillation from raspberries, thirty kilogrammes yielded, however, only 5 grammes. This example

\* Arch. der Pharm. Bd. 13, s. 248.

may show us how extremely small the quantity of ethereal oil must be (if we except the compounds of ethyl and amyl), found in many wines, since raspberries are a peculiarly fragrant fruit, and the most aromatic grapes scarcely possess  $\frac{1}{100}$  part of the aroma of the raspberries.

Let no one imagine that since fresh wine is not fragrant, it cannot therefore contain odoriferous substances, and that all odoriferous ingredients must necessarily be products of fermentation. We have already remarked that the juice of many grapes is fragrant before fermentation, but that the young wine contains excess of œnanthic ether, which makes it offensive, and apparently causes young wine to affect the head, and less of it can be borne, and a free indulgence in it produces very uncomfortable feelings. This fetid œnanthic ether masks at first the fragrance of the aromatic ingredients. It is not till the wine has been some time in store, and other fragrant ethers have been engendered from œnanthic ether, that the original aroma of the grape juice reappears, being no longer masked, but having its bouquet increased by other aromatic ingredients.

This fundamental fact that fetid œnanthic ether is first formed, and masks all other aroma, is true not only of ethereal oils, which pre-exist in grape juice, but also of those fragrant ethers which we have treated of above. These are sometimes found in the fusel oils of younger wines, sometimes in those of bad wines.

They are found at an early period, though in no very large quantities; but they cannot impart aroma to wine until the greatest portion of the œnanthic ether is decomposed. Œnanthic ether is generally supposed to occasion the vinous odour; but the truth is, it spoils the bouquet, and although it gives rise to many of the aromatic ingredients of cellared wine, so long as it predominates in the wine it is by no means fragrant.

A thorough knowledge of chemistry is not sufficient to explain everything which concerns the aroma of wine. It is well known in pharmacy and perfumery that fresh distilled waters have not a pleasant smell, particularly if they are prepared from fresh plants. They obtain the fragrance which characterizes them after the lapse of time. We need not here look for the formation of a new substance, but rather for the decomposition of one, or for a combination yielding a less agreeable odour, so that the original odour disappears at once. All waters freshly distilled from plants have at first a disagreeable smell.

I may further remark that competent judges are well able to distinguish between the scent of a distilled water, *aqua menthæ* (peppermint water), for example, prepared by distillation, or by dissolving peppermint oil in water. Chemistry here finds its boundary: in both cases it finds peppermint oil and water, and nothing more, at least it cannot with certainty determine the cause of the difference.

The same holds good with respect to the delicate



aroma of wines, differing widely from each other. Brandy, which according to Schubert\* is added to Port wine in the proportion of one-twelfth, may at first be detected by its smell. This Port wine is allowed to lie three years before it is produced, and by that time the smell of brandy has vanished—this is likewise true of substances naturally existing in wine, which also require time to accommodate themselves, if I may use the phrase, to the other bodies present there.

Among the series of fusel oils nothing is known of the substances which appear in rum and other distillates of fermented liquids. Rum is the product of fermented cane-sugar syrup, arrack of rice flour resolved into sugar, and moutwyn of wheat flour converted into sugar. Rum and arrack have a peculiar smell and taste, which depends as much upon fusel oil as that of Cognac and moutwyn, although under other circumstances. Cherry water is a proof how dependent the distillate of a spirituous liquid is upon its origin. Payen † observes rightly that all kinds of starch, such as potato-flour, sago, arrowroot, the flour of different kinds of corn, &c., have a distinctive fragrance, which they owe to a volatile substance peculiar to each.

When, after the starch has been converted into sugar, alcohol is produced from these substances by

\* Pogg, Ann. Bd. 77, s. 197, 397.

† Comptes Rendus, tom. xxiii. p. 489.

fermentation, and the spirit distilled off, the bodies which impart odour must either be decomposed, or contained in the destillate.

According to Faber \* the bouquet of wine is much improved by ethereal oil, which is found in the vine blossoms, and best imparted to the wine by collecting the blossoms which fall when shaken, drying them carefully, and putting a little packet filled with them into the must—or, by distilling the blossoms with alcohol, and adding a little of the destillate to the wine. This method was recommended by Linnæus, on the ground that the flavour of a Smyrnian wine had been much improved by it. The Greek wines, according to Faber, generally have ethereal oil of vine blossoms added to improve their bouquet.

In speaking of the odoriferous ingredients of wine and their origin, ferment oils must be mentioned, although neither their properties nor origin are accurately known. They teach us, however, to direct our attention to something besides fatty or other acids in combination with oxide of ethyl or other such like substances.

Büchner first spoke of such ferment oils. He crushed the plant *Gentiana centaurea*, let it stand some time in water, and then distilled the liquid, whereby an oil was obtained differing entirely from that obtained by distilling the fresh plant with water.

\* Polyt. Centralbl. 1854, s. 1533.

In the same manner a ferment oil has been obtained from the leaves of the *Quercus robur*, having an agreeable odour and a specific weight of 0.795. Bley prepared another ferment oil out of *herba millifolii*, having properties differing from that prepared from the fresh herb. 22 Dutch lb. gave 20 grammes; another kind of oil was obtained from *herba echii*, 24 Dutch lb. yielding 80 grammes. Another from *Urtica urens*,  $\frac{1}{2}$  loth ( $\frac{1}{4}$  oz.) from 46 lb. of the herb in blossom. One also from the leaves of *Salix*, *Plantago*, and *Chærophyllum sylvestre*.

All these ferment oils have a strong odour.

According to Rossignon, from the pressed juice of reinettes and other apples, a ferment oil is obtained which smells like musk.

The production of volatile aromatic substances by the fermentation of plants is universal, and the grape skins are perhaps as well suited to produce it as the constituents of the grape juice itself. But no satisfactory examination has been made with respect to grapes. At any rate these ferment oils deserve to be compared with the fusel oils.

The following observation deserves consideration in so far as it concerns the bouquet of wine. If aromatic wine be distilled out of a retort a brandy is obtained having a pleasant smell, but which will never have the smell of wine. However fragrant the wine may have been, that which remains in the retort after distillation will always smell disagreeably of *œnanthic*

ether. If now the brandy which has been distilled over be added to the liquid remaining in the retort, the original vinous smell is not regained, the bouquet is destroyed.

However carefully the distillation has been carried on in closed vessels, some portion of a very volatile substance has escaped.

Geiger has observed that after some years such a mixture regains its bouquet, a proof that it arises from a substance previously extant in wine.

Schubert\* endeavoured to investigate this subject in another way. He evaporated wine, till only one-fifth of its original volume remained, and then confined it in a bottle. At the end of five years this liquid, which contained from 3 to 4 per cent. acid, had a bouquet like that of wine 100 years old. To me it seems very strange that wine entirely free from alcohol should nevertheless possess vinous odour. Aroma may have been produced in the wine mentioned by Schubert, but since the alcohol was completely expelled, one can hardly imagine the formation of ether to occur.

Schubert is of opinion that the aroma of wine is a product of the action of tartaric acid on wine extract, and that alcohol has nothing to do with it. This view is entirely opposed to the fact, that many compounds of oxide of ethyl appear among the odoriferous constituents of wine.

\* Pogg, Ann. Bd. 77, s. 197, 397.

## CHAPTER XXV.

### ANALYSIS OF WINE.

It cannot be out of place to give some short directions as to the manner of analysing the components of genuine wine, that is, to indicate simple analytical means which are available for every kind of wine.

I suggest two methods of investigation: 1, that of reagents alone, whereby, when an adulterated and genuine wine are compared, the existence of many ingredients may be recognised; and 2, the use of chemical means, by which the various constituents may be separated from each other. We will treat of this last method first.

*Ashes.*—The evaporated wine is burnt. It is not easy to burn the ash white. By the use of the usual reagents, potash, soda, lime, magnesia, in some wines traces of iron, and according to some analyses alumina may be found. Also, chlorine, sulphuric, phosphoric, silicic acid. But these may be passed by.

*Organic ingredients.*—Alcohol and water need not be mentioned.

The other volatile ingredients are either easily or

sparingly volatile. Those which are easily volatile may, according to Fauré's method, be partly detected by smell, and in this manner should large quantities of aromatic wine be ever examined, substances hitherto unknown may perhaps be obtained in perceptible quantities. We have already treated of these and the more sparingly soluble in speaking of the odoriferous constituents of wine.

We must now direct our particular attention to the non-volatile organic bodies.

Acetate of lead may here be carefully employed, being first added as a neutral, then as a basic salt; then ammonia may be added, and the lead may ultimately be removed by means of sulphuric acid.

A satisfactory result may be obtained by this simple method.

I will shortly indicate the object to be attained by it. If sugar of lead be added to wine, the colouring matters, fatty oils, tannic acid, albuminous matters, tartaric and other vegetable acids (acetic acid excepted), phosphoric and sulphuric acids, and part of the chlorine will be precipitated.

As all wine has an acid reaction (if only from cream of tartar), an acid liquid flows from the neutral acetate of lead which has been added, it contains free acetic acid, and a portion of colouring matter is more or less soluble in it, as are also tartrate, malate, and phosphate of lead, and especially chloride of lead. Tannate, albuminate, and sulphate of lead are inso-

luble. If the precipitate be washed, still more of the above-named substances are dissolved.

If to the liquid which has filtered off, basic acetate of lead be added, the precipitate will first contain the insignificant amount of colouring matter which has passed through, and then the non-volatile vegetable acids, the trace of phosphoric acid and chlorine, and also a portion of the gum contained in wine.

If the liquid be again filtered, and ammonia be added, a third precipitate is obtained, containing the sugar and the rest of the gum.

If this be now put into a filter, and sulphuric acid dropped in, in order to precipitate the lead, and the precipitate then separated, a liquid remains in which organic bodies which had not previously been precipitated are found, together with potash, soda, magnesia, and lime.

We have thus three precipitates, the first produced by sugar of lead, the second by basic acetate of lead, and the third by basic acetate of lead and ammonia.

After these precipitates have been well washed, they are suspended in water and sulphuretted hydrogen passed through them, filtered, the liquid warmed, in order to expel the excess of sulphuretted hydrogen, and again filtered.

Three liquids and three separate amounts of sulphide of lead are thus obtained, of which the third contains nothing, the second a little colouring matter,

and the first, procured from the precipitate of sugar of lead, a copious amount of colouring matter, together with fatty acids.

We will give an example of analysis of wine conducted in this manner, pure Bordeaux being used for the purpose.

Red Bordeaux was precipitated with sugar of lead, and the precipitate, a dirty pale blue, placed upon a filter and washed. A violet red liquid passed through the filter. After that which remained upon the filter had been suspended in water, sulphuretted hydrogen was passed through it. The filtered liquid was pale red. After evaporation it deposited a little sulphide of lead, which was filtered off. After further evaporation it remained of a bright red colour.

Besides a portion of red colouring matter, tannic acid, albumen, tartaric, racemic, and malic acid might be contained in the liquid, supposing them to exist in the wine.

Neither gum, sugar, nor extractive matter could be found in the liquid in question, but sulphuric, phosphoric, and a trace of muriatic acid, though the last would be principally contained in the precipitate of basic acetate of lead.

A diluted solution of chloride of iron indicated strongly the presence of tannic acid in the red liquid concentrated by evaporation.

When nitric acid was added to another portion of the liquid in which the tartaric acid had been



neutralized by an alkali, it gave rise to a white flocculent precipitate, which, as all other substances possibly existing, are soluble in nitric acid, can be nothing else but albumen. This would be proved by the solubility of the precipitate in alkali, as well as by the yellow colour (Xantho-proteic acid) which it acquired under the influence of nitric acid and ammonia.

If a portion of the original liquid be evaporated to dryness, and heated with hydrated-potash, copious fumes of ammonia were developed, which coloured red litmus paper blue. The presence of albumen was thereby proved.

In the original liquid chlorine gave a flocculent precipitate of albumenchlorit.

The following means were employed to determine the other organic acids :

A part of the liquid was mixed with milk of lime, and filtered. The precipitate caused by the milk of lime being dissolved in muriatic acid and ammonia, tartaric and racemic acid were easily detected (p. 248).

Another portion of the liquid was mixed first with acetate of lime, then with ammonia, and afterwards filtered. The liquid which flowed through was warmed, but no precipitate of citrate of lime was formed; nor did filtration and addition of alcohol give rise to a precipitate of malate of lime (p. 249).

After carbonate of ammonia and ammonia had been added, the liquid was warmed and filtered. After evaporation the clearer liquid left a trace of a brown

substance, which was too insignificant in quantity to allow of its qualities being investigated (compare the precipitate of basic acetate of lead with this and ammonia further on). The sulphide of lead obtained from the precipitate of neutral acetate of lead has been treated in detail under the colouring matter of wine (p. 216), so I pass over it, and the fatty acid also spoken of—

2. Basic acetate of lead was now added to the violet red liquid obtained from the precipitate of sugar of lead. Another precipitate, but weaker than the former, was obtained; its colour was grey.

Placed upon a filter, a colourless liquid flowed from it. The precipitate was washed with water, suspended in water, and sulphuretted hydrogen passed through it.

The precipitated sulphide of lead being placed upon a filter, the liquid that flowed from it was colourless, so that the small amount of colouring matter still existing remained in the sulphide of lead. This, however, was not examined, as nothing else could be contained in it.

The liquid that had flowed from the sulphide of lead was warmed in order to expel the excess of sulphuretted hydrogen. It was colourless, but evaporation turned it first yellow, and afterwards brown.

After alcohol had been added to the liquid which was not evaporated, a milk-white fluid was formed, which at last became clear, and deposited a substance

which appeared to be gum. Not a trace of pectin, or any substance derivable from it, could be perceived (p. 38).

Racemic acid was not present, for a precipitate was not formed till after a portion of the acid liquid had been saturated with ammonia, and solution of gypsum added to it.

Lime-water was mixed with another portion of the liquid. It gave rise to a copious precipitate of acid tartrate of lime. The tartaric acid of this salt was held in solution partly as tartrate of lead by the excess of acetic acid in the fluid which was filtered from the precipitate formed by the sugar of lead.

Another portion of the liquid was mixed with milk of lime, tartaric acid combined with the lime, it was filtered, and then carbonic acid gas was conducted through it and warmed.

When ammonia was added to the liquid which flowed from the tartrate of lime, and this warmed, no precipitate of citrate of lime was produced. When alcohol was added it gave rise to a precipitate of malate of lime.

Citric acid does not, therefore, exist in this wine, but malic acid appears in the lead precipitate.

After evaporating what remained of the liquid a very small portion of a brown substance was left, which was not reducible by means of the test solution of oxide of copper and potass, and could not therefore be glucic acid. It was precipitated with basic acetate of

lead, and dissolved in excess of the same. The quantity was very insignificant, not sufficient to allow of its properties being examined, a process which would probably be difficult in any case.

3. To the liquid which flowed from the precipitate of basic acetate of lead, basic acetate of lead together with ammonia were again added. A yellow flocculent precipitate was obtained. After this had been suspended in water, sulphuretted hydrogen passed through it, and filtered, a liquid clear as water was obtained, which was freed by being warmed from sulphuretted hydrogen and ammonia.

No precipitate was obtained by adding basic acetate of lead to a portion of this liquid ; so that no glucic acid in a form which allows of precipitation exists in it.

Test solution of oxide of copper and potass indicated at once and without trouble the existence of sugar (uncrystallisable sugar), which when exposed to evaporation is speedily transformed into glucic acid.

Besides sugar and a trace of an organic substance, which (as in the liquids previously mentioned) became more and more coloured when exposed to evaporation, there was nothing present except a little gum, indicated by precipitation with alcohol.

The sugar is so very easily decomposed that its solution cannot be evaporated without becoming dark-coloured and passing into glucic acid ; so that basic acetate of lead mixed with the solution gives

rise to a voluminous precipitate, which when further evaporated is resolved into apo-glucic acid.

If therefore the object be to obtain the sugar, and not to form from it glucic acid, evaporation must not be employed. Knowing how very easily the sugar existing in red wine is resolved into glucic acid, I have carefully sought for this acid, but in vain. I think it probable that the small quantity of brown substance found in the liquid obtained from the precipitate of sugar of lead and basic acetate of lead, contains apo-glucic acid (p. 253).

If glucic acid be contained in wine, it escapes analysis by resolving itself into apo-glucic acid, even when it is precipitated with lead salts. It is well known that glucate when exposed to the air is speedily transformed into apo-glucate. Here, where only a little exists, the transformation must be very rapid. Not only the precipitate of sugar of lead, but likewise that obtained from basic acetate of lead and ammonia become darker when exposed to the air.

What Scheele calls "extractive matter," contains, after becoming brown, apo-glucic acid; it is a product of sugar which first passes into glucic acid, and when exposed to the air becomes brown and decomposed.

4. The liquid obtained after the separation of the precipitates with sugar of lead, and basic acetate of lead and ammonia, was freed from lead by sulphuric acid. Potash, soda, lime, and magnesia might exist in it,

but neither sugar nor glucic acid. All acids, and many other bodies were removed from it.

Evaporation rendered the liquid dark brown, so that some organic substance must be contained in it. It was proved, however, to be neither sugar nor glucic acid, since when warmed with potash it did not turn brown. Lime water occasioned no precipitate; sugar of lead formed no precipitate in it, but basic acetate of lead did. Nitrate of silver, when saturated to excess with ammonia, gave a reduction of silver. But this did not decompose the test solution of oxide of copper and potass.

It would be superfluous here to seek after the doubtful substance which figures under the name of extractive matter, and with which we are quite unacquainted. Its amount is insignificant.

If we now consider what we have found, setting aside the inorganic substances and volatile bodies, we have the following substances—red colouring matter, tannic acid, albumen, racemic, and tartaric, but no citric acid, malic acid, gum, no pectin, uncrystallisable sugar, a brown substance deducible in part from a small amount of glucic acid existing in the wine, besides extractive matter, which cannot at present be more accurately described. This sketch must be rendered complete by special examination of each of those substances, which may be separately obtained in the way I have indicated.

## CHAPTER XXVI.

### THE METHOD OF DISTINGUISHING WINES BY CHEMICAL REAGENTS.

WHEN simple means are employed to detect adulterations, they serve at the same time to establish the genuineness of the wine, and may therefore be considered here. Comparisons serve to test a wine that is suspected, and to determine the nature and quantity of many of its constituents. We here give some of the reactions of different wines as the foundation of a simple method of determining adulteration.

We have taken several kinds of wine by way of comparison: red wines—Port, Burgundy-Beaune, Hermitage, Langlade and Tavella (two very pale red wines); further, Burgundy-Pommard, Roussillon, and St. George; wines not red—Bordeaux-Sauterne, Champagne, Madeira, Teneriffe, Rhine, Muscat, Lachryma Christi, white Bergerac, and white Côtes.

In every instance the same quantity of wine was measured off, and either a portion, or at the end of the experiment, an excess of the same reagent was added.

If chloride of iron be added to an equal quantity of wine, it indicates tannic acid in the following pro-

portions :—white wines : in Bordeaux-Sauterne hardly any colouring, in Champagne a perceptible tinge, but nothing more. Then follow Teneriffe and Madeira. A decidedly perceptible colouring was visible in Rhine wine. White Côtes, white Bergerac, Muscat, and Lachryma Christi were rendered much darker.

Among the red wines (old) Port was least affected ; then came Tavella, Hermitage, Langlade and Burgundy-Beaune ; those most coloured were Bordeaux, Burgundy-Pommard, Narbonne, Benicarolo, Roussillon, St. George.

Isinglass added to white wines gave rise to no precipitate in Bordeaux-Sauterne ; none perceptible in Teneriffe and Madeira ; a very weak one in Rhine, Champagne and Muscat, Côtes, and white Bergerac wine ; a copious one in Lachryma Christi.

Among red wines, Port was least precipitated, Burgundy somewhat more, Tavella and Hermitage still more 'decidedly ; Langlade, ordinary Bordeaux, St. George, Burgundy-Pommard, Narbonne, Benicarolo and Roussillon most of all.

Chlorine water mixed with white wine, formed a precipitate in Muscadel, Bordeaux-Sauterne, Rhine wine, white Côtes, white Bergerac, which was considerable in Teneriffe, Madeira, and Champagne, most so in Lachryma Christi. Among red wines Tavella, Langlade, and Port wine were most discoloured ; next Burgundy and St. George ; then Hermitage, Bordeaux, Burgundy-Pommard, Narbonne, Benicarolo, and last



of all Roussillon. After the decomposition of blue colouring matter, Tavella, Langlade and Port wine are rendered least turbid by a yellow precipitate; then come in rotation, Burgundy, Bordeaux, Hermitage, Burgundy-Pommard, Narbonne, Roussillon, Benicarlo, the last of which are very turbid.

Nitrate of silver added to white wine forms a very small precipitate in Champagne and Rhine wine; none in Muscadel, Madeira, white Côtes, white Bergerac, Bordeaux-Sauterne; in Teneriffe more, and most of all in Lachryma Christi. In red wines, a very small precipitate is formed in Bordeaux, Burgundy, Port, Hermitage, Tavella, Langlade, Burgundy-Pommard, St. George, a larger one in Narbonne, Benicarlo, Roussillon. They are all somewhat diminished by the addition of nitric acid, the precipitate of Burgundy-Pommard most so, being almost re-dissolved, whilst much chloride of silver remains undissolved in Benicarlo.

Ammonia makes all white wines brown, Champagne, white Côtes, and white Bergerac least so; Bordeaux-Sauterne, Madeira, Teneriffe, Rhine wine, Muscadel more so; and Lachryma Christi quite brown.

Among red wines, ammonia gives the colour of Rhine wine to Port and Tavella. In the following wines it gave rise to a dirty brown green precipitate, least in Burgundy, more in Hermitage, and most in Bordeaux, Langlade, Burgundy-Pommard, St. George, Roussillon, Narbonne, Benicarlo. In all of them the

liquid is brown. The effect of ammonia upon all red wine is to make the colour fade into blue, then into green, and only when there is excess of ammonia does it become brown (p. 220).

Chloride of barium in white wines—Champagne is least precipitated by it; next come Muscadel, Madeira, Teneriffe, Bordeaux-Sauterne, Lachryma Christi, Rhine wine, and white Côtes, and white Bergerac.

Among red wines, Port, Bordeaux, Burgundy, and Hermitage, give the least precipitate; above these come, gradually increasing, St. George, Langlade, Burgundy-Pommard, and still above, Tavella, Narbonne, Roussillon, and Benicarlo. An addition of nitric acid diminishes the precipitates, and the residue remains as sulphate of baryta, the proportions ranging in the following order:—Champagne deposits least, then come Muscadel, white Côtes, white Bergerac, Bordeaux-Sauterne, Madeira, Teneriffe, Lachryma Christi; Rhine wine leaves the largest amount.

In the red wines Port leaves the least; then come St. George, Burgundy-Pommard, Bordeaux, Burgundy, Hermitage, Langlade, Tavella, Narbonne, Roussillon, Benicarlo.

Oxalate of ammonia in white wines—Champagne gives the smallest precipitate; then come Bordeaux-Sauterne, Rhine wine, Muscadel, Madeira, Teneriffe, Lachryma Christi, white Bergerac, and white Côtes.

Of the red, Langlade gives the smallest precipitate, then increasing gradually, St. George, Bordeaux, Bur-

gundy, Port, Hermitage, Roussillon, Burgundy-Pommard, Narbonne, Benicarolo.

Sugar of lead, in white wines, invariably occasions a flocculent precipitate—least in *Lachryma Christi*, rather more in Champagne, Muscadel, and Bordeaux-Sauterne, still more in Rhine wine, Madeira, and Teneriffe, and most of all in white Bergerac, and white Côtes.

Among red wines, Port gives the smallest precipitate of a dirty brown colour, Tavella a more copious dirty white one, Burgundy, Langlade, a very abundant pale blue violet like, still more copious and darker blue violet is yielded by Hermitage, Burgundy-Pommard, and Benicarolo; Bordeaux, St. George, Narbonne, and Roussillon give a voluminous pale blue precipitate.

All precipitates are soluble in nitric acid, which makes the red wines bright red.

Alum in white wines produces no precipitate, makes the red wine redder, otherwise there is no change. If potash be carefully added, so that the alumina is not precipitated by it, a precipitate of alumina more or less coloured appears in the white wines.

In the red wines, in Tavella a dirty precipitate, in Port wine and St. George a dirty brown, in the others a dirty blue precipitate, but entirely dependent upon the quantity of alum and potash which are added; so that when a good deal of alum is added, the precipitate may be violet, or even pale red. This reaction must therefore be entirely rejected.

## CHAPTER XXVII.

### ADULTERATION OF WINE.

THE great variety of different kinds of wine renders it evident that it will never be possible to give definite chemical characteristics by means of which each kind can be analysed with the view of ascertaining their genuineness. On the other hand, it is certain that wines with peculiar and settled names, ought to coincide in their principal qualities, and that when such is not the case a definite cause must exist which explains the difference.

Chemistry is in a position to detect a great many of these adulterations. But to maintain that it is able to detect every adulteration would be a complete mistake. It is bad enough that in proportion as science advances, and is more able to detect adulteration, means are discovered of multiplying such adulterations.

It is maintained without hesitation that Port wine is prepared in England, which experienced chemists take for Port, and which yet contains not a drop of Port wine. I should like for once to see such Port wine, and know too whether it really possesses the aroma

and flavour of good Port. England is notorious for its manufacture of wine, and London especially appears to be the seat of the so-called "wine brewery."

This manufacture is principally carried on in the sweet wines, which, as a rule, are more easily imitated than others. But other wines are also imitated. It is well known that the quantity of Port and Madeira drunk in England is larger than that imported. Cape wines, which are not much prized in England, are especially used for the manufacture of wine. As they are sweet, ferment is added to set the sugar fermenting, by which process many of the properties peculiar to Cape wines are withdrawn. Colouring and aromatic ingredients are then added to the fermented liquid, and thus Portuguese, Spanish, and French wines are counterfeited. Madeira, Malaga, and Alicant, are imitated by fermenting sweet Languedoc wine, and adding aromatic and colouring ingredients; and this is so well known in our country, that it is universally acknowledged that we drink very little genuine Madeira, because there are such numerous imitations which bear this name.

Many of those who are of opinion that the most ordinary wines are generally adulterated, look upon wine with great distrust. Much depends here upon what is understood by adulteration. I place myself unconditionally on the side of those who consider everything added to, or taken from the fermented grape-juice (even the clearing it with albumen or

isinglass, or the addition of substances containing tannic acid in order to supply a deficiency of that acid), as adulteration. But as it is not generally so understood, I have no right, much as I regret it, to put this interpretation upon the term.

I must also distinguish between adulterations, such as are supposed to be allowed, and those which are universally looked upon as fraudulent. It is obvious that such a distinction is purely arbitrary, and

Wine is adulterated:—

1. When aroma is added in order to give the appearance of age to young wine.
2. When cane or fruit sugar is added to sweeten it.
3. When means are used either to withdraw a portion of tartaric acid from the wine, or to neutralize free acetic acid.
4. When alumina or sulphuric acid is added, which generally is accompanied by the simultaneous addition of sugar, in order to improve the flavour of the wines.
5. When colouring ingredients are added to imitate stronger-coloured wines.
6. When inferior wines are mixed with others.
7. When water is added to strong wines.
8. When alcohol is added to weak wines.

In general, the addition of any substance with a view to obtain some property peculiar to a good wine—the counterfeiting wine by preparing it by means of wine ferment or other ingredients obtained from wine, or indeed out of other substances that are indepen-

dent of grapes—the forcing carbonic acid gas into sweet wines, to imitate effervescing champagne.

One of the first adulterations which must be named has won for itself a respectable name, that of blending. It ought not to be called adulteration if two or three wines of the same kind are mixed together in order to represent a wine of a general name, without any other addition; for example, to an aromatic wine a second which is stronger, and a third which is weaker. He who orders Bordeaux wine, and gets two or three kinds mixed together, in the manner mentioned above, is truly and honestly dealt by. An acquaintance with the art of blending is a capital method of satisfying the taste of consumers, and of producing an article suited to exportation and cellaring. Claret is such a mixture of wines of uncertain names.

There are plenty of wines which, though not themselves agreeable, mix very well. When wines of the same kind are mixed, and no new name given them, it cannot be called adulteration. But when the name is altered, even supposing good wine to be used, the person who does it is guilty of falsehood, and untruth is falsifying, and adulteration is cheating, and he who cheats is an impostor.

It is, indeed, no easy matter to restore its right name to an adulterated wine: chemically to distinguish Cantemerle from Johannisberg, or Lafitte from Madeira, cannot be required; but what is desired is to know if Cantemerle be really Cantemerle.

We should speak untruly if we maintained that science is able, by comparing an adulterated with a genuine wine of the same name, to prove that the adulterated wine was made in imitation of the genuine wine.

Such things cannot be required from science, because no single kind of wine is exactly the same year after year; and also to express it as accurately as possible, because the composition of no two grapes in the whole vineyard is exactly alike.

But if such kinds of wine as are distinguished in trading (and it is usual now to give different names to wines produced from vineyards lying close together) were always of uniform composition, there would still be such resemblance between the sorts that are related as would render chemical discrimination impossible. A trifling difference in the time of the vintage, in the care with which the grapes are gathered, in pressing, in the size of the fermenting vats, and in many other details, may occasion varieties perceptible to the senses, but connected with no real chemical difference. There may even be a difference in chemical composition, but in such wines as we speak of this difference would be less than exists between different kinds of wine.

In such case the chemist, with his eyes open, finds himself in the same position as the genuine connoisseur of wine with his eyes shut—both make mistakes, and take *a* for *b*.

I say this to shield science from the friendly reproach sometimes levelled at her, that she cannot do



everything. Neither can the best prover of wine do everything by bringing the constituents together.

I may remark, in general, that in cases where this adulteration is undertaken with a view to give a particular character to wine, and where inferior and better sorts are mixed, this mixture must be compared with pure wine, and their ingredients analysed, especially the inorganic, which appear to be most important. The qualities of wines grown in particular places are generally peculiar and constant.

All that is here said refers equally to wines of the first, second, and third quality, having a peculiar mark, whether cellared or not.

When we consider the endless variety which obtains among wines produced in places lying near together, we must also observe that so great a coincidence may be found between wines produced in very different places as to allow of their being mistaken for one another. We need scarcely consider it strange, since it is a fact, that two or three causes of variety—quality of soil, temperature, and kind of grape—seem, instead of supporting, to cancel each other, by restoring a kind of equilibrium. Constantia and the *Vin de Paille*, of Hermitage, are examples of great resemblance. If the difference be great when the wine is young, time will sometimes remove it, as is plainly proved by Muscadel, Frontignac, and Malaga.

We have already seen (p. 49) that some kinds of grapes are dried before wine is prepared from them,

by which means an increase is effected in the saccharine contents, and indeed in the contents of all the ingredients of the wine to be prepared, and also that the same end is obtained when the grape-juice is partially concentrated by evaporation. Those who call wines prepared in this manner adulterated, because they are not simply fermented, consider all Tinto and Malaga wines as adulterated.

At other times the grape-juice is not evaporated, but sugar, whether cane or fruit is indifferent, added to it; the cheapness of potato syrup causes it to be very much employed in this way (p. 51). No one can deny that this is adulteration. And yet this method of preparation is so commonly resorted to in unfavourable seasons or in places where the grapes are not sweet, that it has ceased to be considered adulteration. The sugar ferments and makes the wine richer in alcohol, but only sweeter if a great deal of sugar is added. It is impossible at a later period to detect that sugar has been added.

Oenologists say, "Only take care that your potato syrup is free from copper and gypsum, and then it is no adulteration."

In the preparation of Madeira, Port, and other kinds of wine, an addition of brandy is employed. This is at first perceptible to the taste, and can only thus be detected. Alcohol is alcohol, and as a rule that which is added is prepared by distillation from the same kind of wine, but of rather an inferior

sort. No one can separate it artificially, and if after a time the addition is able to combine with the ingredients of wine it is no longer perceptible to the taste. Nor can it ever be proved that alcohol has been mixed, since no one can lend his palate to another.

If now Madeira produces a grape which yields 14 per cent., and it is always estimated at 17, then 3 per cent. may be mixed with it, and after a time it will not be discernible.

A mixture of alcohol can only be conclusively inferred, if an excessive quantity has been mixed, and there is no reason why this should be done.

The adulteration of wine, particularly strong wine, with alcohol is by no means uncommon; it is also added to weak wines to increase their strength, and to such as have become acid, and had their acid neutralised by carbonates of potash, soda, and lime.

The quantity of alcohol may be absolutely too great, or just sufficient, even when an addition has been made to it, for example, in wine that has become acid. If much acetate of potash and 11 per cent. alcohol are co-existent in red Bordeaux wine, it may be assumed that as much alcohol has been added as was abstracted for the formation of acetic acid. If, for instance, acetic acid combined with potash amounts to  $\frac{1}{2}$  per cent., and 11 per cent. alcohol is still found, it is impossible to determine whether  $\frac{1}{2}$  per cent. alcohol has not been mixed in, because the amount of alcohol in any kind of wine is not constantly the same.

The amount of alcohol in wine varies as much as 1 or 2 per cent.; in stronger wines, as Port, Madeira, &c. up to 3 per cent. (p. 176).

It is a very general idea that wines have something added to them, and yet the prejudice against the addition is as general. As if the alcohol added differed in any respect from that which naturally exists in the wine! It is not the interest of the adulterator to add too much, and if he only add as much as is usually contained in the wine—then alcohol is alcohol. I cannot imagine that this prejudice is founded on an opinion expressed by Fabroni, that no alcohol exists in wine, but that it is first *formed* (not *separated* from it), by distillation (a view which has been expressly refuted by Brande); for how could it have obtained such universal currency?

As to the effect on the body produced by wine, there can be no difference between wine containing 10 per cent. alcohol, and wine of the same kind in which 7 per cent. alcohol exist, and to which 3 per cent. are added.\*

The same holds good of a stronger wine, to which water is added to diminish its strength. At first it is perceptible to the taste, but after a time it combines more intimately, and unless too much has been added, can no longer be discerned.

In both cases, when either alcohol or water have

\* At first the taste is different, but long practice alone can distinguish between them when the addition has lately been made.

been added, examination by chemical methods is impossible, unless the limits by which the composition of a particular kind of wine are regulated have been overstepped. The attenuation which the addition of water causes all the ingredients of wine (alcohol excepted) to suffer, can never be sufficient to allow of a perceptible chemical difference between them and those in undiluted wine; if it were so, taste would decide the matter, for we have said that a certain variety exists in the amount of different constituents common to wines of the same character, and we have shown this in detail in respect of 4 wines; Port, Madeira, Teneriffe, and Rhine (p. 165).

Experienced wine tasters find, however, a great difference if water *and* alcohol have been mixed. In this case it may easily happen that all the non-volatile components sink below the minimum of what is usually found in genuine wine of the same kind.

With respect to these two additions (alcohol and water), I may just observe that in order to determine their presence, comparison with a normal wine of the same kind is necessary, and that not only with respect to the quantity of alcohol, but also of the non-volatile ingredients. Such an analysis must therefore include, a determination of the specific gravity of the wine, of the specific gravity of the wine freed from spirit and restored to its original volume by means of water, of the alcoholic contents (the other two estimates serve to determine this, p. 159); evaporation of the wine, and

determination of the solid substances remaining after evaporation, of the ashes of the wine, and the use of such reagents as indicate chlorine, sulphuric acid, lime, &c. &c. All this must be effected in order to compare the quality of the wine to be analysed with a pure example of the same sort.

It will always remain doubtful whether alcohol or water have been added, as long as the limits of the normal composition of wine of the same quality have not been passed.

The determination of the colour, smell, and flavour, must be combined with the foregoing, but these subjective impressions cannot furnish any proof.

Among the less objectionable adulterations we must consider the employment of means to lessen the too great acidity of young wine; as pulverised chalk or marble, gypsum, clay, or other substances, for the purpose of clearing, not discolouring, the wine; also, the addition of a little tannic acid to preserve wine which threatens to become ropy; the addition of albumen, isinglass, gluten and tannic acid, cream or milk, either to clear wine or to make it darker. I call many of these adulterations, though they are not generally so considered.

A comparative examination would sometimes enlighten us upon these matters. Isinglass, albumen, tannic acid, whether added immediately or later, and cream, are so completely precipitated that they may be sought for in vain afterwards.

The same may be said of clay or sand when used for clarifying.

Chalk or marble added to young wine for the purpose of withdrawing excess of tartaric acid cannot afterwards be detected; the superfluous tartaric acid combines with a portion of lime added to it, and is precipitated, whilst any excess of chalk remains undissolved. The case is different when wines that have become acid have their free acids removed by means of chalk, potash, or soda. The alkali thus used remains in the wine, and if a mixture is to be called adulteration it is one.

If potash or soda is used to saturate the acetic acid in wines which have become acid, a small excess of alkali will first alter the colour, and the flavour will never be as good as before. The wine becomes sharp and salt. The acetic acid has been produced from the alcohol of the wine, and in order to make the wine sufficiently strong, alcohol must be added at the same time as the carbonate of potash. This adulteration is proved to have taken place, if when the wine has been evaporated, and the residue distilled with sulphuric acid, a great deal of acetic acid is obtained. (In pure wine the acetic acid is free.) Or the wine is evaporated to dryness and treated with alcohol. Alcohol of 53 per cent. dissolves acetate of soda; of 95 per cent., acetate of potash. If chalk has been employed to combine with the acetic acid, the wine gives a copious precipitate with oxalate of ammonia, whilst genuine wine yields very little precipitate.

Lead is now never used to adulterate wine. Sugar is often used to mask acetic acid ; but sugar is present in all wine ; it is only therefore by estimating the saccharine contents in good wine of the same kind that it can be discovered whether a ponderable quantity of sugar has been added.

In any case the distillation of the wine gives the excess of free acetic acid. It must not be forgotten that all wines contain a certain amount of free acetic acid which is obstinately retained by the wine extract (p. 244).

If wine be evaporated, and the extract that remains be found to contain free tartaric acid, no acetate of potash, soda, or lime can be present.

The presence of alum, which is occasionally added to red wines to heighten their colour, may be ascertained by burning the ashes of the wine extract obtained by evaporation. First a larger amount of ashes, next more sulphuric acid, and lastly, more alumina, are found in such wines.

Lime and common salt have already been mentioned (p. 99).

Liebig recommends the addition of neutral tartrate of potash in order to free wines from excess of tartaric acid. Cream of tartar is thus formed, which crystallizes and is deposited. Although an adulteration, this method is preferable to any other ; 3·5 grammes (54 grains) of this salt were required for 1 litre (1·8 pints) of old wine of 1811.



Batilliat prescribes a very opposite treatment for Burgundy, and recommends 1 gramme, (15·4 grs.) of tartaric acid, to every litre (1·8 pints) of wine, by which means the wine is said to retain in a high degree the capability of bearing exportation to a warm climate (p. 130).

Lassaigue has made the observation that from  $\frac{2}{1000}$ ths to  $\frac{3}{1000}$ ths sulphuric acid are often mixed with French wines. This may be partially ascertained by the use of chloride of barium and nitric acid, but this method cannot be entirely depended on, as by the sulphurising of the wine sulphurous may be resolved into sulphuric acid. The method recommended by Lassaigue is also incomplete. Half a strip of paper must be dipped in wine and then thoroughly dried; what has been dipped in the wine will be carbonised by the concentrated sulphuric acid. But potash, lime, and magnesia are also in the wine. The sulphuric acid added will saturate these bases and set free tartaric and even phosphoric acid. Unless more sulphuric acid has been added than these bases can take up, Lassaigue's test will be useless. From 0·2 to 0·5 per cent. ashes are found in various wines (p. 293), and from 0·1 to 0·3 per cent. sulphuric acid may well be taken up in some kinds without a trace being indicated by Lassaigue's test.

The best of all plans is comparison with a good kind of wine, either by determining the amount of sulphuric acid, or by nitric acid and chloride of barium; or by diluting with water, which generally suffices. If

the volume of the wine has been trebled by water, and the same amount of turbidity is produced in genuine wine by chloride of barium as is perceived in the diluted adulterated wine, then we may assume that the adulterated wine contains three times as much sulphuric acid as the genuine. This rough computation is quite satisfactory in such a case. It is still, however, a question, how much of this sulphuric acid must be ascribed to sulphurising.

Adulteration with colouring matters is very common, especially when red wine is prepared from white wine, and from currants, darker from light wine, and also when the object is to impart to one sort of wine the shade peculiar to some other kind. Also in cases of spoiled wine.

Strangely enough, people have endeavoured to detect adulterations by means of reagents which were to act upon the colouring matter, and have not even selected for this end the safest and most characteristic. But even if the colouring matter have been tampered with, it is no proof that the rest of the wine is adulterated.

Indeed it is not very difficult to separate the colouring matter of wine in the manner detailed (p. 218), and then to re-act upon it. And those who will not take the trouble to do more than to add alumina and potash to the wine, to see what comes of it, are not fit to give an opinion upon adulteration.

In the meantime much has been written about the colour which precipitates from genuine red wine ought

to have, and yet nothing can be more uncertain. It is everywhere asserted that the precipitate of sugar of lead in red wine, if pure, must be green, whereas it is really dirty pale blue. The mistake seems to have arisen from an alcoholic extract of purple grape skins being used instead of a watery extract. If purple grape skins be extracted with alcohol, a red tincture is obtained, as when water is used. Whether it be that a little tartaric acid clings to it, or that a little acetic acid is formed, it is certain that the colour is not blue, but bright red.

Sugar of lead gives rise in this alcoholic extract to a green precipitate; and causes a dirty pale blue precipitate in the watery extract. If  $\frac{1}{2}$  of alcohol be added to the watery decoction, a blue precipitate is obtained. It must therefore be blue in pure red wine. The reason the precipitate obtained by acetate of lead from the alcoholic solution of purple grape skins is green, is that it is the product of a blue and of a yellow precipitate; for blue and yellow give green. The cause of this I cannot explain, it does not depend upon the colouring matter of wine, but upon another substance extracted by means of alcohol from the grape skins.

We generally see that a very red tincture of purple grape skins and alcohol turns pale in a few hours, and acetate of lead then gives rise to a green precipitate in it. Ammonia does not produce a blue, but a greenish yellow colour in this pale red alcoholic tincture.

When such changes take place in the reaction of an alcoholic extract from purple grape skins, no con-

fidence can be felt in the reaction of the wine, even when it is perfectly genuine.

I must acknowledge that I do not give full confidence to any of the reactions recommended for detecting foreign colouring matters, and I therefore dismiss them from consideration. They only serve as indications to those who are very expert in analysing wine. I add the following observations, without laying any great weight on them, in order to complete what is already known respecting this matter, and I repeat that the pure colouring matter must be separated, its relation to other substances analysed, and a comparison instituted between it and such foreign colouring matters as are generally used.

Jacob\* has observed, respecting the colouring matter of red wine, that adulteration with the juice of elderberries cannot be detected by basic acetate of lead, if the juice has been previously fermented.

Wines of Tonnerre he chiefly examined with alumina and carbonate of ammonia, and obtained the following precipitates :

	Alumina and carbonate of ammonia.	Sugar of lead.
Natural wine .....	Grey.....	Blue grey.
The same with logwood .....	Dark violet ....	Weak dark blue.
Brazil wood .....	Carmine, rose..	Wine red.
Poppy .....	Slate grey ....	Dirty grey.
Dwarf elder ( <i>sambucus ebulus</i> ) ..	Bright violet ...	Blue grey, or beautiful green.
Elder ( <i>s. nigra</i> ) .....	Blue grey ....	Dirty green.
Cornellian cherries ( <i>cornus masc.</i> )	Light green....	Dirty green
Litmus .....	.....	Blue green.

\* Journ. de Ch. Méd. 1844, Févr. p. 92.

The colour of the precipitate yielded by the fruits of the dwarf elder and sugar of lead, varies according to whether the juice is fresh or fermented. The precipitate from the fresh juice was blue grey, the liquid beautiful violet, the precipitate from the fermented juice beautiful bright red.

It has been suggested by Ness von Esenbeck to add an equal volume of solution of alum (1 part to 12 parts water), to the wine, which makes the colour bright red; then a solution of carbonate of potash, but so that all the alumina shall not be precipitated. After twenty-four hours the colour of the precipitate must be compared with that of the genuine wine, which gives a dirty grey more or less reddish precipitate. If the wine was coloured with Brazil wood, the precipitate will be rose coloured; if with logwood, grey violet; with cherries, beautiful violet; with the fruit of the dwarf elder, violet; with bilberries, blue grey; with poppies, grey brown. Other varieties may also be observed when excess of potash is added to pure wine.

Batilliat proposes to add ammonia to red wine. The colouring matter then becomes brown, and if tartaric acid be now put to it the colour of genuine wine will not be restored, though that caused by artificial colouring matters may. He is of opinion that potash cannot be used instead of ammonia, because, although it turns the wine brown, the original colour may be restored by means of tartaric acid. When the potash used was stronger, or had acted for some time, this was not the case.

Pélouze and Fremy assert that basic acetate of lead gives rise in pure wine to a grass greenish precipitate, which is blueish if extract of logwood has been added, and indigo, if Brazil wood has been employed.

Filhol recommends adding, first ammonia and afterwards sulphide of ammonium. All genuine red wine will become green, and that which has been artificially coloured blue red, or violet.

Müller declares that carbazotate of potash gives a dirty precipitate in genuine red wine, and produces a crimson colour without precipitate in such as has been coloured by means of poppies.

Vogel says that sugar of lead occasions a precipitate, which is green grey in genuine wine, indigo blue if the wine has been adulterated with Brazil wood, elder, or bilberries, and red if the wine has been coloured with logwood, sandal-wood, or beet-root. The wine itself becomes colourless if the colour is caused by logwood or bilberries, but remains red if elder-berries have been used.

Vogel also says, that if potash be added to wine which has been coloured with Brazil wood it yields a red-brown colour, and becomes green if bilberries or elder-berries have been used.

Chevallier considers the discolouration produced by potash as unsatisfactory, since the alterations occasioned by it vary according to the age of the wine.\*

Lime-water gives rise to a precipitate which is

\* Journ. de Ch. Méd. Juin 1827, p. 306.

yellow-brown in pure red wine, red-brown in wine coloured with Brazil wood; green in that coloured with bilberries and elderberries; and yellow, but capable of being reddened by acids, in that coloured with beet-root.

• Orfila gives the following reactions:—

	Solution of Alum.	Protonitrate of Tin.	Chloride of Tin.
Bordeaux . . . . .	Dark bronze colour..	Dirty blue ..	Dark blue.
Burgundy . . . . .	The same . . . . .	Same . . . . .	Dark green grey.
Wine coloured with bilberries } . . . . .	Dark olive green ..	Grey . . . . .	Dark steel green
Dwarf elder . . . . .	Bright olive green..	Grey green..	Bottle green.
Cornelian cherry..	Dark green . . . . .	Grey . . . . .	Grey brown.
Logwood . . . . .	Very dark, and a precipitate } . . . . .	Violet . . . . .	Dark brown.
Brazil wood . . . . .	Violet red . . . . .	Same . . . . .	Dark brown red.
Litmus . . . . .	Blue red . . . . .	Bright blue..	Dark blue.

Nothing more need here be said; comparison renders it sufficiently clear that many so-called means of detecting are really methods of concealment. What one calls green another looks upon as blue; in short things go on here as they generally do in the world. Upon such uncertain grounds Chemistry can pronounce no certain decision.

The great variety of colour which the same reagent gives, may be ascribed partly to difference in the age of the wine, and the treatment it has undergone, partly to the incompleteness of the technical language of colour (a defect which science is continually combating), and partly to the fact that the chemist's eyes

are subjective. The peculiarity of colour depends upon the eye, not upon the light.

That aromatic ingredients are very generally used to improve the quality of wine is a fact we cannot conceal. Ask the druggists how much acetic ether they sell to the wine dealers.

In our country these adulterations have not yet been practised to any great extent; in England they are far beyond us. But we may prepare ourselves for a terrible future, for so soon as an acquaintance with oxides of ethyl and other combinations which occur in wine spreads, we may expect a new series of adulterations of wine with aromatic ingredients. Insurmountable difficulties will be opposed to their detection; and if nothing has been used except what may possibly exist in wine, the only means of discovering adulteration will be to analyse the relative proportions (as already shown in the case of alcohol and water), and such a proceeding would be very far from easy.

Batilliat, who has written a book upon wine, to which we have referred several times, does not hesitate to put nitric acid and nitric ether into wine (p. 117). The first speedily darkens the wine, giving it a colour which would otherwise be imparted by time (*pelure d'oignon*); the other gives wines the aroma of the golden reinette—the smell of sweet spirits of nitre.

Although he possesses a vineyard he sees nothing improper in selling such wine, and in general, in making wine as liqueurs or beer is made. If his



business as wine dealer—he is also a druggist—he dishonourable, he is at least honest in confessing it—since he thus puts people on their guard, and enables them to purchase wine elsewhere. His book shows what is done to wine in France.

*Raisin wine.*—In England, where people seem to like being led astray in matters of this kind, wine is prepared from raspberries, mangel-wurzel, plums, and even from beer. The most innocent preparation is that from currants or raisins, and we will say a few words about it, passing by in silence all the other fruits named—since in our country no one would allow fermented liquids from such fruits to be set before him for wine.

Raisin vinegar is made and sold at a few stivers the bottle; for twice the sum a bottle of raisin wine may be procured sufficiently strong, and which must indeed resemble wine, since it is prepared from dried grapes.

I have more than once been assured that raisin wine is prepared and drunk in our country. Many even assert that the quantity used is considerable. Whether or no this be true, it is certain that raisins are dried grapes, and if they are softened in rain water (in which scarcely a trace of a foreign substance is perceptible), pounded, and exposed to sufficient heat, the ingredients of the raisins will be dissolved by the water, and fermentation will produce a wine which chemistry cannot distinguish from genuine wine; nor will it ever be able to distinguish between them, since

the grapes when dried only suffer loss in water, and this can be restored to them afterwards.

If the raisins have been made from white grapes, the wine is white, and it is customary to add a little ferment from red wine, out of which the red colouring matter is extracted, and this gives the raisin wine the colour of genuine red wine. When sufficient care has been taken to maintain such a proportion between the water, raisins, and colouring matter of wine ferment, as exists in the wine which is imitated, chemistry is unable to detect the difference; flavour and aroma can alone decide.

*Currant wine* (dried currants).—Brandy is prepared in Greece from a currant wine, which is also drunk there undistilled. This custom has spread so much that in 1852, 55 million litres of currants were collected in the Peloponnesus.

As the wine prepared from these differs entirely from our ordinary wines, we need not suspect that it is sold among us.\*

In Portugal a particular kind of wine called Vinho Geropica or Vinho Anglica is prepared without fermentation, and highly esteemed. The juice of very carefully selected grapes, either purple or white, is taken, and the moment fermentation begins allowed to run into a cask, a fourth part of which is filled with pure brandy. The fermentation is immediately stopped,

\* Arch. der Pharm. Bd. 70. s. 292, u. Bd. 57, s. 167, in which the method of preparing Greek wines is treated of.

and as soon as the wine has been long enough in the cask to get clear it is bottled off.

Deyeux recommends the following method of detecting adulterations effected by means of cider and perry: The wine is evaporated in order to allow the cream of tartar to crystallise; the process is repeated as long as any of this salt deposits. The taste of the residue is like that of apples and pears; and the smell of apples and pears is distinctly perceived if the extract be thrown upon a coal fire. The same result is obtained if sulphuric acid be added.

Neither tartar nor tartaric acid is found in cider and perry—the absence of these substances is a sign that the liquid contains no grape-juice. The adulterator may however know this, and add the necessary amount of cream of tartar to the cider or perry. In any case the fraud may be detected by warming with ammonia, and adding acetate of lime; for tartrate of lime is insoluble, citrate of lime is soluble, in ammonia, but may be precipitated, if warmed with ammonia whilst alcohol precipitates malate of lime from the filtered liquid.

Cider contains a large amount of tannic acid, and is prepared from sweet apples. It is well known that if sweet apples be cut with a steel knife, the blade will speedily furnish tannate of iron (ink); also that the tannic acid of sweet apples when brought into contact with air is rapidly converted into apothema, so that peeled apples quickly turn brown. Sweet apples when

dried are on the same account always brown. An iron salt added to cider will, therefore, always indicate the excess of tannic acid, unless the adulterator has removed too much by means of isinglass.

Made wines are prepared from the cheapest sugar, that is potato syrup, dissolved in water and mixed with ferment, to which other substances are added, in order to imitate this or that kind of wine. The yeast of beer or wine, and sometimes the crushed grapes, are used as ferment. It is clear that in this manner natural wines may to a great extent be imitated. Crushed currants, cherries, and other fruits, are also often employed as ferment.

I do not, however, think it advisable to write more upon this subject, and so to propagate the knowledge of adulterations. Receipts for made wines are sufficiently common; I will not repeat them here.

## CHAPTER XXVIII.

### FRUIT WINES.

SINCE the name "wine" no longer designates exclusively fermented grape-juice, but is applied to the fermented juice of other fruits, I must not be entirely silent respecting such fruit wines as are more or less used here and in other countries.

The juice of every fruit which contains sugar contains also albumen in larger or smaller quantities. Those influences which bring about fermentation cause this albumen to ferment and to yield a liquid which contains alcohol, water, and the ingredients of the fruit-juice in a state of decomposition (just as in the case of grape-juice), ingredients which necessarily vary according to the nature of the fruits employed.

Cider, perry, currant-wines, &c., are obtained in this manner. The juice of the sweet fruits thus employed is generally less rich in sugar than are grapes, and consequently, even when (as in the case of currant-juice) any sugar is added before fermentation, fruit wines contain less alcohol than wine. They almost all contain malic, not all citric acid.

*Cider.*—Sweet apples, and those generally not the best, are used for this; they are crushed, and what is expressed is mixed with water, and crushed again in order to make a second kind. Apple-juice contains, on an average, 12 per cent. sugar. The juice ferments slowly, and effervescing wine may be prepared from it by bottling it before it has finished fermenting. Bohemia and the North of France are cider countries.

*Perry.*—Pear-juice has, on an average, scarcely 8 per cent. sugar, and, if no sugar is added to it, gives an insipid wine. Apple and pear-juice are often mixed, and allowed to ferment together.

*Plum-wine.*—Plum-juice may contain 20 per cent. sugar. The juice is not always expressed, but the plums are pounded, or allowed to ferment together. The wine is then of an ugly brown colour.

*Cherries.*—Sweet cherries may contain 18 per cent., other kinds less. This wine is also prepared, not from the juice alone, but from the crushed fruit freed from kernels.

*Currant-wine.*—The juice contains about 12 per cent. sugar. Black, white, and red currants are used for this wine. Their great acidity and small saccharine contents render the addition of sugar necessary; but when it is added largely, a strong, but unwholesome wine, is obtained.

*Raspberry-wine.*—The juice may contain 10 per cent. sugar, but the wine is too acid.

Birch, maple, and cocoa-nut wine are obtained by

fermenting the juices of the respective plants; and cane-sugar and mangel-wurzel wine may be prepared in the same manner.

Honey-wine,\* or mead, is prepared in Poland, Galicia, and some other parts, from honey, water, and ferment.

A far more detailed and profound treatise might be written upon every one of these fermented liquids than that which I have here given to the reader, upon genuine wine.

\* Balling. Gahrung's Chimie.





# APPENDIX.

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## ON THE ACIDITY, SWEETNESS, AND STRENGTH OF DIFFERENT WINES.

*(From the Proceedings of the Royal Institution of Great Britain.)*

BY  
THE EDITOR.

In the Philosophical Transactions for 1811 and 1813, Mr. Brande has given a table of the strength of wine, beer and spirits : if these fluids acted on the system only as stimulants, no further experiments would be required to enable any one to determine their comparative medicinal and dietetic values ; but wine and beer contain many other substances besides spirit and water. Acids, sugar, ethers, salts, and colouring matter are all also present in varying proportions ; and it must at least be known which wine or beer is most sweet, and which is most acid, as well as which is most strong, before any satisfactory answer can be given whether port or sherry, claret or champagne, bitter beer or brandy should be taken. It would also be very desirable that the amount of salts and volatile ethers should also be known ; but the large quantity of fluid requisite for the analyses renders the questions relative to these substances still more difficult to answer.

I.—*On the Acidity of different liquids.*

Hitherto, though acid is as invariably present as alcohol, very few observations have been made on the acidity of different wines. In Dr. Henderson's work on wine, Dr. Prout has given four determinations of the amount of acid in Rhine wine.

	Tartaric acid by weight in an ounce of wine.
Johannisberger, 1788	contained 4·1 grs.
Rudesheimer, 1811	" 2·7 grs.
Rhenish	" 4·6 grs.
Same	" 4·4 grs.

Professor Liebig, in a paper on Australian wines, gives—

Verdeilho and la Follie	" 2·1 grs.
La Follie and Muscat	" 2·6 grs.
White Muscat Lunel	" 2·8 grs.
Verdeilho	" 2·5 grs.
Riesling	" 1·2 grs.
Irrewang, Pineau Noir, Tinta	} " 2·2 grs.
Pineau gris	
Irrewang white	" 2·9 grs.

Fresenius, in the *Annalen der Chemie*, 1847, gives—

Hattenheimer	" 2·4 grs.
Marcobrunner	" 2·3 grs.
Steinberger	" 2·1 grs.
Choice Steinberger	" 1·8 grs.

For determining the amount of acid stated in the following tables, a standard solution of caustic soda was prepared, so that each division of the graduated tube contained 0·15 grs. of caustic soda; a thousand grain bottle was filled with the fluid to be examined; it was then weighed, and the quantity of test alkali necessary for neutralisation was determined by Clarke's test paper. In the accompanying tables, the acidity, although manifestly due to the presence of several acids, is by calculation reduced to the standard of tartaric acid in an ounce of

fluid. The particular wines and the number of each kind will be afterwards stated.

The following general results were obtained :

The quantity of alkali required to neutralise a measure equal to 1000 grs. of water was—

In Port wine	.	.	.	2·10 grs. to 2·55 grs.
In Sherry	.	.	.	1·95 to 2·85
In Champagne	.	.	.	2·40 to 3·15
In Claret	.	.	.	2·55 to 3·45
In Madeira	.	.	.	2·70 to 3·60
In Rhine wine	.	.	.	3·15 to 3·60
In Burgundy	.	.	.	2·55 to 4·05
In Moselle	.	.	.	2·85 to 4·50
In Geneva	.	.	.	0·07
In Whiskey	.	.	.	"
In Brandy	.	.	.	0·15 to 0·60
In Rum	.	.	.	0·15 to 0·30
In Pale Ale	.	.	.	0·90 to 1·65
In Stout	.	.	.	1·35 to 2·25
In Porter	.	.	.	1·80 to 2·10
In Cider	.	.	.	2·85 to 3·90

Hence proceeding from the least acid wine to the most acid we have Sherry, Port, Champagne, Claret, Madeira, Burgundy, Rhine wine, Moselle. The least acid fluids examined were Geneva and Whiskey ; then Rum, Brandy, Ale, Porter, Stout ; the wines were all more acid than the malt liquids.

The nature of the acid was not absolutely determined, but a volatile acid distils over from wine, which is not acetic acid ; and the action of polarised light shows that tartaric acid is seldom present ; hence the fixed acid is most probably racemic, and perhaps malic acid.

## II.—*On the Sweetness of different liquids.*

That sugars are of different kinds is easily seen by the different effects of the same test ; but the most delicate test of all is polarised light. There are three different kinds of sugar, which when present in different solutions in equal

quantities rotate the polarised ray in different degrees and directions. Cane sugar rotates the light to the right  $\longrightarrow$  and if treated with acid for a few minutes it is entirely changed into sugar which rotates to the left  $\longleftarrow$ . This is called uncrystallisable sugar; for if the solution be even evaporated to dryness, it is changed into sugar which again rotates to the right  $\longrightarrow$ . This sugar is called grape sugar or glucose, and this sugar undergoes no change when again treated with acid.

By means of the saccharometer of Soleil, the degree of rotation to the left or right can be measured, and thus the quantity of sugar in a solution can be determined; with cane sugar alone the results are probably perfectly accurate. With the other sugars the results are not yet so fully established: still at least the minimum amount will be obtained. It is essential that the fluids to be examined should be decolorised first with one-tenth of a solution of subacetate of lead, and afterwards, if requisite, with animal charcoal.

Previous to the determination of the quantity of sugar present in these liquids, when decolorised, they were examined by other tests for sugar, by the sulphate of copper test, by the liquor potassæ test, and with the polariscope. I found no Sherry, Port, Madeira, or Champagne that did not contain more or less uncrystallisable sugar; (two samples of sherry excepted, which were free from any sugar.) I met with no Claret, Burgundy, Rhine, or Moselle wine, (excepting only one sample of Sauterne,) which was not free from every kind of sugar. Usually spirits contain no sugar; but one specimen of genuine French brandy had some cane sugar added to it. All kinds of Ale, Porter, and Stout contain much glucose. Hard cider I found also to be perfectly free from sugar. Sweet cider contained uncrystallisable sugar.

The particular results will be given in the Tables; the general results may be here stated.

	Degrees.		Amount of Sugar in an ounce of fluid.	
In Sherry the sugar varied from	2 to	9	← =	4 grs. to 18 grs.
Port . . . . .	8 to	17	.. =	16 to 34
Madeira . . . . .	3 to	10	.. =	6 to 20
Malmsey Madeira . . . . .	28 to	33	.. =	56 to 66
Tokay . . . . .	37		.. =	74
Samos . . . . .	44		.. =	88
Paxarete . . . . .	47		.. =	94
Cyprus . . . . .	51		.. =	102
Champagne . . . . .	3 to	14	.. =	6 to 28
Sweet Cider . . . . .	9 to	22	.. =	18 to 44
Bitter Ale . . . . .	12 to	130	→ =	12 to 130
Porter . . . . .	23 to	40	.. =	23 to 40
Stout . . . . .	45 to	64	.. =	45 to 64

The fluids examined may be arranged in the following order, commencing with those which contain no sugar, and ending with the most saccharine :

Geneva, Rum, Whiskey, Claret, Burgundy, Rhine, Moselle. These have no sugar. Brandy, Sherry, Madeira, Champagne, Port, Cider, Porter, Stout, Malmsey, Ale, Tokay, Samos, Paxarete, Cyprus.

### III.—On the Strength of different liquids.

Having determined the acidity and the sweetness, the strength of these fluids was the next object of experiment. This was effected by an alcoholometer, invented by M. Geisler, of Bonn, which depends on the tension of the vapour of the fluid to be examined forcing up a column of mercury. To show how nearly the results obtained by this instrument agreed with those obtained by the ordinary process of distillation, comparative experiments were made on the same wine. Thus :—

	By distillation (Mr. Witt) per cent. by measure.	By Alcoholometer per cent. by measure.
Port, 1834 . . . . .	22·46 . . . . .	{ 23·2 } { 23·5 } 20·7
Sherry, Montilla . . . . .	19·95 . . . . .	20·6 20·6
Madeira . . . . .	22·40 . . . . .	{ 23·5 } { 23·2 } 11·1
Haut Brion Claret . . . . .	10·0 . . . . .	11·1 11·1
Chambertin . . . . .	11·7 . . . . .	13·2 13·0
Low quality Sherry . . . . .	20·7 . . . . .	21·1 20·9
Brown Sherry . . . . .	23·1 . . . . .	23·0 23·3
Amontillada . . . . .	20·5 . . . . .	21·0 21·0
Mansanilla . . . . .	14·4 . . . . .	15·4 15·4
Port, best . . . . .	20·2 . . . . .	21·1 21·0
Marcobrunner . . . . .	8·3 . . . . .	9·7 9·5
Home Ale . . . . .	6·4 . . . . .	7·0 7·1
Export Ale . . . . .	6·4 . . . . .	7·0 6·9
Strong Ale . . . . .	9·0 . . . . .	{ 10·7 } { 10·8 }

Generally it may be stated, from my experiments, that the alcohol varied—

	Per cent.	to	Per cent. by measure.
In Port from . . . . .	20·7		23·2
Sherry . . . . .	15·4		24·7
Madeira . . . . .	19·0		19·7
Marsala . . . . .	19·9		21·1
Claret . . . . .	9·1		11·1
Burgundy . . . . .	10·1		13·2
Rhine Wine . . . . .	9·5		13·0
Moselle . . . . .	8·7		9·4
Champagne . . . . .	14·1		14·8
Brandy . . . . .	50·4		53·8

	Per cent.	Per cent by measure.
Rum . . . . .	72·0	77·1
Geneva . . . . .	49·4	.
Cider . . . . .	5·4	7·5
Bitter Ale . . . . .	6·6	12·3
Porter . . . . .	6·5	7·0
Stout . . . . .	6·5	7·9

The particular kinds of wine or beer examined as to acidity, sweetness, and strength, are recorded in the following tables:—

TABLE I.

PORT.	Tartaric Acid per ounce.	Sugar per ounce.	Alcohol per cent.	Specific gravity.
A. quality from importer . . . . .	4·0 grs.	22 grs.	{ 21·1 } { 21·0 }	993·2
A. quality . . . . .	4·2	18	{ 21·3 } { 21·3 }	990·2
General . . . . .	4·0	20	{ 21·0 } { 21·0 }	991·8
Low . . . . .	4·3	16	{ 21·7 } { 21·8 }	992·6
Very fine . . . . .	3·6	34	{ 23·2 } { 23·2 }	996·2
Low . . . . .	4·0	24	{ 22·6 } { 22·5 }	1003·4
G. B. Port . . . . .	3·6	28	{ 20·8 } { 20·7 }	996·6
Roussillon . . . . .	5·0	30	{ 20·7 } { 20·7 }	996·6

TABLE II.

SHERRY.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
J. C. . . . .	3·6 grs.	6 grs.	{ 18·5 18·5	990·5
Low light . . . .	3·8	6	{ 21·1 20·9	988·8
Golden low . . . .	4·2	12	{ 23·2 23·2	991·1
Golden better . . . .	4·3	10	{ 21·4 21·4	992·9
General light . . . .	3·7	4	{ 21·1 21·0	988·2
Best . . . . .	3·6	6	{ 21·2 21·1	990·0
Low brown . . . . .	4·5	18	{ 23·0 23·3	997·1
Very low light . . . .	3·4	10	{ 21·8 22·1	987·9
Very low dark . . . .	4·2	12	{ 24·6 24·7	991·2
C. Golden . . . . .	3·6	4	{ 17·4 17·3	988·7
B. Good . . . . .	4·8	16	{ 20·2 20·2	997·0
Light, A quality, Amontillada	3·7	4	{ 20·7 20·6	985·3
B. Amontillada . . . .	3·5	10	{ 17·0 17·0	992·4
F. Amontillada, very good .	3·3	0	{ 21·0 21·0	984·0
B. Mansanilla . . . .	4·3	2	{ 15·7 15·6	987·8
C. Mansanilla . . . .	4·5	6	{ 16·6 16·6	992·2
	4·5	6	{ 16·8 16·8	990·0
T. Mansanilla . . . .	4·3	4	{ 19·3 19·0	988·0
G. Mansanilla . . . .	3·5	0	{ 15·4 15·4	989·2



TABLE III.

MARSALA, MADEIRA.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
Paxarete imported direct, 12 years old	3·6 grs.	94 grs.	{ 18·8 }	1039·9
			{ 18·9 }	
B. Marsala, 1847	4·3	10	{ 21·0 }	990·5
			{ 21·1 }	
I. Marsala	4·3	10	{ 20·0 }	990·9
			{ 19·9 }	
Lisbon	4·8	6	{ 19·0 }	989·0
			{ 19·1 }	
Teneriffe	5·0	8	{ 20·6 }	990·0
			{ 20·7 }	
Madeira 17 years in bottle at Ceylon	5·0	6	{ 19·7 }	991·2
			{ 19·7 }	
Madeira three times in East Indies	4·5	16	{ 19·2 }	996·3
			{ 19·0 }	
Madeira direct	4·8	20	{ 19·1 }	994·8
			{ 19·0 }	
Madeira, Agoa de Mellos	12·0	66	{ 19·8 }	1012·0
			{ 19·8 }	1011·9
Malmsey Madeira	10·0	56	{ 18·8 }	1046·4
			{ 18·7 }	
Tokay	9·0	74	{ 16·0 }	1016·8
			{ 16·0 }	
Samos	10·8	88	{ 15·1 }	1050·1
			{ 15·0 }	
Cyprus	10·8	102	{ 15·4 }	1041·4
			{ 15·5 }	
Shiraz	5·0	16	{ 18·3 }	996·8
			{ 18·4 }	

TABLE IV.

CLARET AND BURGUNDY.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
T. Medoc	5·0 grs.	0 grs.	{ 9·4 }	995·4
			{ 9·1 }	
L. and S. Medoc, 24s.	5·8	0	{ 9·7 }	995·1
			{ 9·6 }	
Medoc, 36s.	5·3	0	{ 10·0 }	995·3
			{ 9·9 }	
Talbot St. Julien, 48s.	5·3	0	{ 9·1 }	995·3
			{ 9·1 }	
Haut Brion	4·3	0	{ 11·1 }	994·3
			{ 11·1 }	

TABLE IV. *continued.*

CLARET AND BURGUNDY.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
Claret, 60s. . . . .	4·8 grs.	0 grs.	{ 10·5 } { 10·5 }	994·4
Chambertin, 84s. . . . .	4·3	0	{ 13·2 } { 13·0 }	993·0
Macon (red), 40s. . . . .	5·5	0	{ 10·5 } { 10·4 }	994·4
Grave (white), 42s. . . . .	6·8	0	{ 10·1 } { 10·1 }	997·4
Sauterne, 72s. . . . .	5·5	5	{ 13·6 } { 13·5 }	996·7
B. Sauterne . . . . .	6·8	0	{ 14·5 } { 14·3 }	998·1

TABLE V.

HOCK, MOSELLE, CHAMPAGNE.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
Rudesheimer, 1834 . . . . .	5·3 grs.	0 grs.	{ 11·7 } { 11·7 }	994·3
Marcobrunner Cabinet, 1818	6·0	0	{ 9·7 } { 9·5 }	996·5
Steinberger, 1846 . . . . .	5·3	0	{ 12·9 } { 13·0 }	992·5
Geisenheimer, 1842 . . . . .	5·8	0	{ 10·6 } { 10·6 }	994·9
MOSELLE.				
Brauneberger, 1842 . . . . .	7·6	0	{ 9·4 } { 9·4 }	995·3
Scharzhofberger, 1843 . . . . .	4·8	0	{ 8·7 } { 8·7 }	995·3
CHAMPAGNE.				
Sillery Mousseux, Première qualité . . . . .	4·9	24	{ 14·8 } { 14·7 }	1011·8
		24		
Sparkling, 48s. . . . .	4·6	28·	{ 14·3 } { 14·1 }	1021·7
		28		
Moet's first quality, 1846, 80s.	5·2	24	{ 14·5 } { 14·4 }	1014·2
		24		
Moet's Still dry Sillery, 1842, 110s. . . . .	4·0	6	{ 14·5 } { 14·5 }	989·2

TABLE VI.

SPIRITS, LIQUEURS.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
Best Brandy . . .	1.1 grs.	4.4 grs.	{ 53.6 } { 53.8 }	930.1
Cheap Brandy . . .	0.27	0	{ 52.0 } { 52.0 }	933.3
Calais Brandy . . .	1.1	0	{ 50.6 } { 50.4 }	932.6
Cognac . . . . .	1.1	0	{ 52.6 } { 52.4 }	928.9
Thompson's Brandy . . .	1.1	0	{ 51.2 } { 51.0 }	930.8
Best Rum . . . . .	0.56	0	{ 72.2 } { 72.0 }	885.4
Cheap Rum . . . . .	0.56	0	{ 77.1 } { 77.1 }	874.6
Geneva . . . . .	0.18	0	{ 49.4 } { 49.4 }	932.8
Whiskey, Highland . . .	0.18	0	{ 59.4 } { 59.2 }	915.5
Noyau . . . . .	0	150	{ 29.4 } { 29.4 }	1159.4
Curaçoa . . . . .	0	?	{ 46.0 } { 46.0 }	1101.8
Maraschino . . . . .	0	120	{ 36.8 } { 37.0 }	1113.1

TABLE VII.

CIDER From Stockland, near Honiton.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
A. medium quality. Hard best	6.0 grs.	0 grs.	{ 7.5 } { 7.4 }	998.1
B. Hard . . . . .	6.5	0	{ 6.8 } { 6.8 }	1001.3
C. Hard . . . . .	5.8	0	{ 6.0 } { 6.0 }	998.5
D. Hard . . . . .	5.0	0	{ 7.1 } { 7.1 }	999.0
L. Sweet . . . . .	6.2	18	{ 6.8 } { 6.7 }	1005.2
W. Sweet . . . . .	4.7	20	{ 5.4 } { 5.4 }	1006.7
S. Sweet . . . . .	5.5	44	{ 6.5 } { 6.5 }	1013.8
N. Sweet . . . . .	5.9	36	{ 6.6 } { 6.6 }	1012.6

TABLE VIII.

PORTER, STOUT.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
Y. Mild Porter . . . . .	3·4 grs.	34 grs.	{ 6·6 } { 6·6 }	1011·0
Bottled Porter . . . . .	3·4	23	{ 6·5 } { 6·5 }	1009·4
Stout . . . . .	3·7	49	{ 9·8 } { 9·8 }	1017·9
Mild Stout . . . . .	3·2	64	{ 8·0 } { 8·0 }	1027·1
N. Porter, 18 months. . . . .	3·2	37	{ 6·7 } { 6·6 }	1011·0
Porter, 3 months. . . . .	3·0	40	{ 7·0 } { 6·8 }	1015·0
Stout 18 months. . . . .	3·7	45	{ 7·8 } { 7·9 }	1014·0
Stout 3 months. . . . .	3·7	60	{ 6·9 } { 6·9 }	1023·7

TABLE IX.

BITTER ALE.	Tartaric Acid per ounce.	Sugar per ounce.	Spirit per cent.	Specific gravity.
T. Pale Ale, Nov. 1852 . . . . .	2·0 grs.	12 grs.	{ 8·1 } { 7·9 }	1003·8
Family Ale, Dec. 1852 . . . . .	1·8	14	{ 6·6 } { 6·6 }	1002·9
Strong Ale, Oct. 1852 . . . . .	2·7	45	{ 10·5 } { 10·5 }	1016·7
Stout, Dec. 1852 . . . . .	2·2	42	{ 8·8 } { 8·8 }	1017·2
S. Pale Ale, March 1853 . . . . .	1·5	45	{ 6·8 } { 6·7 }	1011·8
Pale Ale, Dec. 1851 . . . . .	2·5	35	{ 7·2 } { 7·1 }	1008·6
Pale Ale, strong, Jan. 1853 . . . . .	1·7	103	{ 11·0 } { 10·9 }	1034·6
P. Pale Ale, 5 months . . . . .	1·5	40	{ 7·7 } { 7·5 }	1011·4
Pale Ale, 18 months . . . . .	1·8	30	{ 7·1 } { 7·2 }	1007·8
Arctic Ale, very strong . . . . .	2·7	83	{ 12·4 } { 12·3 }	1023·4
Home Ale . . . . .	1·5	40	{ 7·0 } { 7·1 }	1010·6
Export Ale . . . . .	1·5	43	{ 7·0 } { 6·9 }	1011·7
Strong Ale . . . . .	2·2	100	{ 10·8 } { 10·7 }	1029·2

## ERRATA.

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PAGE	LINE		<i>for</i>		<i>read</i>	
6	15		single		simple	
31	11		contained		is	
32	15		though they may		hence they can scarcely	
34	3		soluble		insoluble	
46	9		oil		acids	
49	last but one		undissolved		undecomposed	
52	2		these are		this is	
64	4		{ everywhere produced		{ more especially is formed	
			{ from vegetable mucus		{ from gluten	
65	1		mucus		gluten	
75	19		ferment		fermentation	
83	23		begun		{ was set up, similar to that	
					caused	
87	5		and		out of	
87	6		and regulated		became aggregated	
89	12		common		distilled	
91	1		white		soft	
91	22		It follows necessarily		{ In consequence of this at	
					least it is observed	
111	5		are altered		decrease	
111	13		or combined with		or changed into	
114	13		with regard to		as is shown by	
116	13		gall extract		gallic acid	
117	8		quercetin		quercitrine	
122	2		50 or 53 F.		10° 4 or 14° F.	
125	15		remains		at first remains	
128	6		are together equal		both correspond to	
131	1		alkali		acetic acid salt	
131	3 from end		enough		at least	
139	13		Burgundy		Bordeaux	

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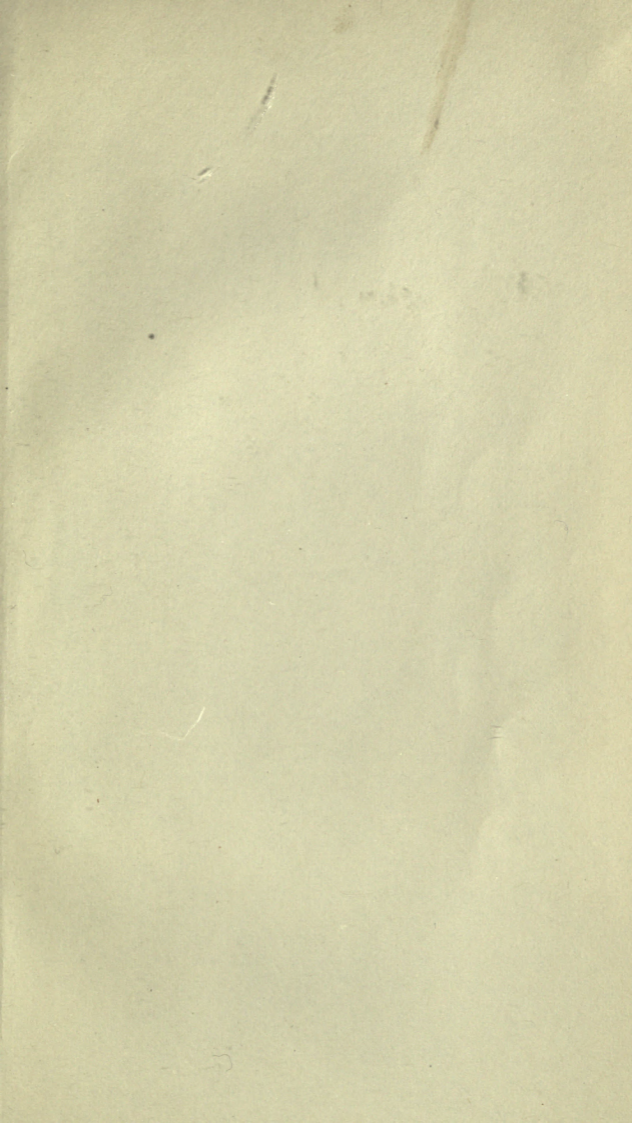
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