

VIII. *An Investigation on the Chemical Nature of Wax.*By BENJAMIN COLLINS BRODIE, *Esq.**Communicated by Sir BENJAMIN C. BRODIE, Bart., F.R.S. &c.*

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III. *On Myricin.*

I HAVE placed the investigation of the Chinese wax between that of the cerotic acid and of the residue of the bees'-wax which remains after that substance has been separated from it. By the saponification of this Chinese wax we procure, as I have shown, an acid identical with the cerotic acid from bees'-wax, and also the alcohol of this acid, so that the chemical history of these substances is closely connected. We have moreover in the Chinese wax to deal with a substance found in nature in a state of great purity, the products of the decomposition of which by alkalies and by heat can readily be prepared and examined. The knowledge of the relation of these products to one another throws great light upon the nature of myricin, which is not a pure substance, and the chemical relations of which are complex.

I have stated that the first extracts of wax with alcohol give with acetate of lead an abundant precipitate in a hot alcoholic solution. This affords us a ready test of the presence of the cerotic acid. The wax may be long boiled with alcohol before the whole of the cerotic acid is removed. If however this process of boiling and decantation be continued, a time will come when the acetate of lead will cease to give any precipitate whatever in the hot alcoholic extract. The residue after this extraction I speak of as myricin. It is advisable to continue for two or three times the operation of boiling and decanting, even after the acetate gives no precipitate, the cerotate of lead not being entirely insoluble in the hot solution.

The myricin thus prepared is a greenish substance of about the consistency of wax, uncrystalline, still possessing a slight smell of wax, and of a melting-point of 64° C. This substance is hardly acted on by dilute potash. It is however saponified by boiling with strong potash, and more readily by an alcoholic solution of the alkali. The saponification may also be effected by melting it with hydrate of potash, as in the case of the Chinese wax. The products are the same in whichever way the operation be conducted.

If the soap from the saponification of the myricin be treated in the same manner as the similar soap from the Chinese wax\*, it also will be found to contain two substances, an acid and another substance which is contained in the ether with which the baryta salt is extracted. On attempting to purify these substances respectively

\* Philosophical Transactions, 1848, Part I. p. 161.

by crystallization out of alcohol, ether or absolute alcohol, great variations in the melting-point both of the acid and of the basic substance will be observed. And careful observation shows that these are not, as in the case of the Chinese wax, substances in a state of comparative chemical purity, but are mixtures, both in the case of the acid and of the other matter, of at least two bodies difficultly separable from one another. It is the separation of these substances which gives a peculiar difficulty to the investigation of the nature of myricin.

Although the acid and basic products of the saponification may thus, as in the case of the Chinese wax, be separated by precipitation of the soap by a baryta salt, in the case of the bees'-wax these substances admit of a simpler method of separation, without which method, so difficult is it to wash perfectly out the baryta salt, that I question whether the substances could be obtained pure. The soap, in whatever way the saponification may have been effected, and after the alcohol, if any, used for the saponification has been distilled off, is to be dissolved in a large quantity of water, and the boiling solution decomposed by an acid. The melted mass which results from this operation, after having been repeatedly boiled out with water, is to be dissolved in a large quantity of hot alcohol. An abundant precipitate appears in the cold fluid from which the solution is to be filtered, and the precipitate repeatedly redissolved and recrystallized out of alcohol. The precipitate will at length be found to consist, almost entirely, of the basic portion of this waxy matter. The alcoholic solution contains the acid.

I shall proceed to give the simplest method by which the pure substances may be obtained, and those experiments which I have made upon their constitution, which I think can leave no doubt upon the mind of the chemist as to the true nature of that matter of which by far the greater portion of the myricin and, indeed, of the wax itself consists.

The first separation of the products of saponification may be made as I have stated, by combining the acid with baryta and washing out the resulting salts with ether; the basic portion of the products may be obtained as pure by this as by the other method.

#### *Melissin.*

If the substance contained in the ethereal solution, with which the baryta salt is washed out, be crystallized out of ether or alcohol, the melting-point will be considerably raised, from below 70° C. to above 80°, by repeated crystallization. The difficulty with which the melting-point was raised, made it evident that the substances contained in the solution were to be separated only by long crystallization and a careful attention to the variations of the melting-points. I made various experiments to discover a satisfactory method of purification. At length I found that if the ethereal solution be filtered while yet warm, and when only a small portion of matter has crystallized out, a substance remains on the filter of a melting-point of 85° C. of a satiny lustre, and of highly crystalline appearance. It is with difficulty that

even a small portion of substance can be thus obtained, and it is necessary to use, during the filtration, a hot water apparatus to prevent the precipitation of the whole matter dissolved. I have never been able to succeed in further raising the melting-point of this body, and therefore regard it as pure. In this condition it crystallizes on cooling from the melted state, and its crystallization is marked by striæ parallel to the line of cooling; it being in all respects, but the melting-point, similar in appearance to cerotin as procured from Chinese wax.

I give this method of preparing this substance as it was the first I adopted, and as it can thus be procured in a high state of purity. I afterwards however discovered the use of rectified coal naphtha as a solvent for these substances, and by far the best and simplest method of procuring the body is by crystallization out of that solvent, of the precipitate from the alcoholic solution which I have before mentioned, as procured by dissolving in alcohol the wax matter obtained by decomposing by an acid the soap from the myricin. By alcohol the basic portion of the saponified myricin is separated from the acids. By naphtha the substance of 85° melting-point is separated from another and probably an analogous body, of which I shall speak hereafter.

This substance gave to analysis the following numbers. The result is the same in whatever way the substance is prepared.

Substance.	CO <sub>2</sub> .	HO.
I. 0·2685 grm. gave . . . .	0·8075	0·341
II. 0·2597 grm. gave . . . .	0·7839	0·3326
III. 0·278 grm. gave . . . .	0·84375	0·35325
IV. 0·2584 grm. gave . . . .	0·7812	0·325
V. 0·2511* grm. gave . . . .	0·7595	0·3215
VI. 0·2617† grm. gave . . . .	0·7870	0·3295

which give in 100 parts—

	I.	II.	III.	IV.	V.	VI.
Carbon . . .	82·02	82·40	82·77	82·43	82·48	82·01
Hydrogen . .	14·11	14·25	14·11	13·97	14·22	13·99
Oxygen . . .	3·87	3·35	3·12	3·60	3·30	4·00
	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>

These analyses agree with the formula—

	Atomic weight.	Calculated.
C <sub>60</sub> . . . .	360	82·19
H <sub>62</sub> . . . .	62	14·15
O <sub>2</sub> . . . .	16	3·66
	<u>438</u>	<u>100·00</u>

This substance I propose to call *Melissin*.

\* This substance was procured directly from wax, from which it may be obtained and purified in the same manner as from the purified myricin; which is the simplest way of procuring the substance if the other products of saponification are not required.

† This substance was procured from the Ceylon wax mentioned in a former paper.

*Melissic Acid.*

Melissin, heated with lime and potash, as the similar experiment was made with cerotin\*, is, like that body, converted into an acid. This acid has a similar appearance to the wax acid already described. It has however a much higher melting-point, namely, 88°–89° C. The preparation of the substance need not be again described.

	CO <sub>2</sub> .	HO.
I. 0·2655 grm. gave . . . . .	0·7764	0·3104
II. 0·2507 grm. gave (another preparation) . . . . .	0·728	0·2507
III. 0·2508 grm. gave . . . . .	0·7333	0·3077
IV. 0·2396 grm. gave (another preparation) . . . . .	0·7026	0·2885
V. 0·258 grm. gave . . . . .		0·3085

which give in 100 parts—

	I.	II.	III.	IV.	V.
Carbon . . . . .	79·74	79·19	79·74	79·97	
Hydrogen . . . . .	13·00	13·32	13·63	13·40	13·28
Oxygen . . . . .	7·26	7·49	6·63	6·63	
	<hr/>	<hr/>	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00	100·00	

These analyses agree with the formula—

	Atomic weight.	Calculated.
C <sub>60</sub> . . . . .	360	79·64
H <sub>60</sub> . . . . .	60	13·27
O <sub>4</sub> . . . . .	32	7·09
	<hr/>	<hr/>
	452	100·00

I prepared the silver salt of this acid in precisely the same manner as was prepared the silver salt of the cerotic acid.

I. 0·6085 grm. gave . . . . .	0·1175 silver.
II. 0·678 grm. gave . . . . .	0·1315 silver.
III. 0·58625 grm. gave (another preparation) . . . . .	0·11575 silver.

which give in 100 parts—

	I.	II.	III.
Silver . . . . .	19·30	19·39	19·74
		CO <sub>2</sub> .	HO.
I. 0·4619 grm. of the salt gave . . . . .		1·0863	0·4464
II. 0·484 grm. of the salt gave . . . . .		1·13375	0·471

giving in 100 parts—

	I.	II.
Carbon . . . . .	64·13	63·90
Hydrogen . . . . .	10·73	10·81
Oxygen and silver . . . . .	25·14	25·29
	<hr/>	<hr/>
	100·00	100·00

\* Philosophical Transactions, 1848, Part I. p. 161.

These analyses lead to the formula  $C_{60}H_{59}O_4Ag$ .

	Calculated.
$C_{60}$ . . . . .	64·38
$H_{59}$ . . . . .	10·55
$O_4$ . . . . .	5·77
$Ag$ . . . . .	19·30
	100·00

The formula therefore of the hydrated acid is  $C_{60}H_{60}O_4$ . This acid I call Melissic Acid.

*Chlor-Metal.*

By the action of chlorine on melissin a perfectly analogous result is obtained to that obtained by the action of chlorine on cerotin. The substance undergoes also a similar change in appearance, being converted into a resin.

The substance was prepared and analysed with a view to confirming the formula of the body.

	CO <sub>2</sub> .	HO.
I. 0·4136 grm. gave . . .	0·589	0·175
II. 0·4263 grm. gave . . .	0·602	0·1835

which give in 100 parts—

	I.	II.
Carbon . . . . .	38·83	38·51
Hydrogen . . . . .	4·70	4·78
Oxygen and chlorine . . . . .	56·47	56·71
	100·00	100·00

I. 0·6663 grm. gave 1·4821 grm. of chloride of silver equivalent to 0·3665 grm. of chlorine.

II. 0·6075 grm. gave 1·341 grm. of chloride of silver equivalent to 0·3316 grm. of chlorine.

III. 0·6475 grm. gave 1·4375 grm. of chloride of silver equivalent to 0·3555 grm. of chlorine.

These determinations correspond in 100 parts to—

	I.	II.	III.
Chlorine . . . . .	55·01	54·58	54·91

These analyses lead to the formula

$$C_{60} \left\{ \begin{array}{l} H_{45\frac{1}{2}} \\ Cl_{14\frac{1}{2}} \end{array} \right. O_2.$$

$C_{60}$ . . . . .	38·50
$H_{45\frac{1}{2}}$ . . . . .	4·86
$Cl_{14\frac{1}{2}}$ . . . . .	54·90
$O_2$ . . . . .	1·74
	100·00

As in the case of the cerotin, by the action of chlorine two equivalents of hydrogen are removed without replacement by chlorine, while the further action is an action of substitution, the substance being the analogue of chloral.

The products of the distillation of melissin are analogous to those of the distillation of cerotin. The substance partly distils over unaltered, and is partly, with the loss of water, converted into solid hydrocarbon. Sulphuric acid also combines with it under the same conditions as with the other wax-alcohol.

*Palmitic Acid from the Saponification of Myricin.*

Melissin is soluble with such great difficulty, in every solvent suitable for washing out the baryta salt from the wax soap, that its separation from the acid cannot in this manner be effected. It may however be separated by simple crystallization. The alcoholic solution (p. 278) from which the melissin has crystallized out, after having been considerably concentrated and again filtered from any precipitate produced on cooling, contains hardly a trace, if any, of that substance. The acids are very soluble in alcohol, and it is only on great concentration that they crystallize from that solvent. The alcohol is to be distilled off to the point of crystallization, and the first portions only of the fat acid selected for the preparation of the pure substance. The acid is to be boiled with potash, combined with baryta, and washed out with ether.

On decomposing the baryta salt with hydrochloric acid, a fat acid separates, having the appearance of margaric or palmitic acid, which latter body is in truth the principal acid of the wax. It is however mixed with another acid of a lower melting-point, for which reason it is desirable, as I have mentioned, to use in its preparation only the first crystallization of the acid. From this other body it is separable with the greatest difficulty; but by long-continued crystallization from ether, an acid may be obtained of the melting-point of 62° C., beyond which point it cannot be raised. This acid gave to analysis the following results:—

		CO <sub>2</sub> .	HO.
I.	0·2486 grm. gave . . . . .	0·6877	0·278
II.	0·2605 grm. gave . . . . .	0·7145	0·290
III.	0·2542 grm. gave . . . . .	0·6937	0·2847
giving per cent.—			
	I.	II.	III.
Carbon . . . . .	75·42	74·80	74·43
Hydrogen . . . . .	12·43	12·36	12·43
Oxygen . . . . .	12·15	12·84	12·14
	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00

The silver salt was made as in the other cases by precipitation from the ammoniacal solution of the acid.

I.	0·6885 grm. of this salt gave . . . . .	0·2005 silver.
II.	0·66025 grm. of the same gave . . . . .	0·1920 silver.
III.	0·623 grm. of another preparation gave . . . . .	0·182 silver.
IV.	0·609 grm. of the same gave . . . . .	0·17625 silver.
V.	0·671 grm. of another preparation gave . . . . .	0·197 silver.
VI.	0·744 grm. of the same gave . . . . .	0·2185 silver.

giving in 100 parts—

I.	II.	III.	IV.	V.	VI.
29·12	29·23	29·21	28·94	29·35	29·36

	CO <sub>2</sub> .	HO.
I. 0·4458 grm. of the first preparation gave . . .	0·869	0·3495
II. 0·4463 grm. of the same preparation gave . . .	0·870	0·3555
III. 0·5896 grm. of the second preparation gave . . .	0·7545	0·3065

which correspond in 100 parts to—

	I.	II.	III.
Carbon . . . . .	53·16	53·22	52·82
Hydrogen . . . . .	8·70	8·85	8·75
Silver and oxygen . . . . .	38·14	37·93	38·43
	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>

The silver salt is by no means insoluble in the ammoniacal solution, so that in the making of the salt by this method a certain separation of the substance is effected. If any impurity were presented, it probably would be detected on analysing the acid as again separated from the silver salt.

	CO <sub>2</sub> .	HO.
I. 0·2523 grm. of the acid thus separated gave . . .	0·6970	0·285
II. 0·228 grm. of the same gave . . . . .	0·6255	0·257

giving in 100 parts

	I.	II.
Carbon . . . . .	75·38	74·82
Hydrogen . . . . .	12·56	12·52
Oxygen . . . . .	12·06	12·66
	<u>100·00</u>	<u>100·00</u>

These analyses, as well as those of the acid previous to combination with silver, agree with the formula of palmitic acid, C<sub>32</sub> H<sub>32</sub> O<sub>4</sub>, with which substance the melting-point of the acid also identifies it. The calculated numbers in parts per cent. of the acid and silver salt are—

C <sub>32</sub> . . . . .	192	. . . . .	75·0
H <sub>32</sub> . . . . .	32	. . . . .	12·5
O <sub>4</sub> . . . . .	32	. . . . .	12·5
	<u>256</u>		<u>100·0</u>
C <sub>32</sub> . . . . .	192	. . . . .	52·8
H <sub>31</sub> . . . . .	31	. . . . .	8·5
O <sub>4</sub> . . . . .	32	. . . . .	9·0
Ag . . . . .	108·1	. . . . .	29·7
	<u>363·1</u>		<u>100·0</u>

*Distillation of Myricin.*

The discovery of the cerotic acid rendered it evident that in order to obtain the products of distillation of myricin, and especially the acids in a state of purity, it was necessary first to remove that body and to distil only the residue of the wax. I give the results of this experiment made with myricin. The first portions of the distillate consist almost entirely of acids, the latter of hydrocarbons. During the distillation a smell of butyric acid may be perceived. This however appeared to me to diminish when the boiling of the wax with alcohol had been very long continued. It is possible to effect nearly a complete separation of the acids and the hydrocarbons by distillation. It is however not advisable to proceed in this manner, but it is best after boiling the distillate with water to saponify the whole by potash. The soap may be removed by a syphon from the hydrocarbons which float on the surface.

*Palmitic Acid from the Distillation of Myricin.*

The acid, having been purified in the usual manner by washing out the baryta salt with ether, and the subsequent methods of purification, presents an appearance similar to the acids obtained by saponification. By crystallization the melting-point may be raised to 62° C.

	CO <sub>2</sub> .	HO.
I. 0·2592 grm. of this acid gave . . . .	0·7165	0·2931
II. 0·250 grm. of this acid gave . . . .	0·6865	0·27925
III. 0·2775 grm. of this acid gave . . . .	0·75925	0·311

These analyses correspond in 100 parts to—

	I.	II.	III.
Carbon . . .	75·39	74·89	74·61
Hydrogen . .	12·58	12·40	12·45
Oxygen . . .	12·03	12·71	12·94
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

The silver salt of this acid, prepared as before, gave the following results:—

I. 0·5006 grm. of the substance gave . . . .	0·1479 silver.
II. 0·2295 grm. of another preparation gave . . . .	0·0685 silver.

which correspond in 100 parts to—

	I.	II.
Silver . . . . .	29·54	29·84

	CO <sub>2</sub> .	HO.
0·3505 grm. of the same salt gave . . . .	0·6873	0·2758

which gives in 100 parts,—

Carbon . . . . .	53·47
Hydrogen . . . . .	8·74
Oxygen and silver . . . . .	37·79
	<hr/> 100·00



These numbers prove the identity of the acid from the distillation of myricin with that obtained from the saponification of that substance (p. 283).

There are great difficulties in the way of obtaining even a sufficient quantity of this acid for the determination of its formula. To obtain even a very small portion of it of which the purity may be relied on, it is necessary to operate on a large quantity of the impure acid: for the preparation of this pure myricin is required, free from cerotic acid, which it is not easy to get in any quantity.

These difficulties have prevented me making any further experiments with this acid, the identity of which however with palmitic acid, as obtained by FRÉMY and STENHOUSE from palm oil, and by STHAMER from Japan wax, is made out. I subjoin, for the sake of comparison, the silver determination of the silver salt of the palmitic acid as obtained by these chemists.

	FRÉMY*.			STENHOUSE†.	STHAMER‡.
Silver, per cent. . . .	29·60	29·23	29·42	29·28	29·51

This acid appears also to be the same as the acid obtained by VARRENTRAPP§ from the oxidation of oleic acid by means of lime and potash, which also had the melting-point of 62° C. The silver determinations of this acid gave as the per-centage of silver,

29·27                      29·45                      29·13,

numbers identical with my own.

#### *Melen.*

It is well known that one of the principal products of the dry distillation of wax is a solid hydrocarbon. ETTLING, who first analysed this substance||, concluded from its melting-point, analysis, and general appearance, that it was identical with paraffin, a hydrocarbon then recently discovered by REICHENBACH in the products of the dry distillation of wood. The wax hydrocarbon has therefore borne the name of paraffin.

This substance was supposed, from the analyses of ETTLING and J. GAY-LUSSAC, to be isomeric with olefiant gas.

Recently, however, this has been contested by LEWY, who analysed paraffin from various sources, and showed it, as he conceived, to contain a larger amount of hydrogen than had been previously supposed. In truth the average of his analyses gave,—

Carbon . . . . .	85·03
Hydrogen . . . . .	14·87
	99·90

numbers inconsistent with the old idea. The question however is, whether M. LEWY experimented with a pure chemical substance, for which there is no guarantee.

\* Liebig's Annalen, vol. xxxvi. p. 45. Silver determinations, V. VI. VII.

† Ibid. p. 52. The mean of five determinations closely agreeing. This acid melted at 60° C.

‡ Ibid. vol. xliii. p. 342. The mean of three determinations.

§ Ibid. vol. xxxv. p. 209.

|| Ibid. vol. ii. p. 259.

My own experiments confirm the analyses of ETTLING, and the constitution originally assigned to the substance, to which theoretical considerations also lead. But I cannot see any reason to believe the wax hydrocarbon to be identical with the paraffin of REICHENBACH. This name of paraffin has been applied indiscriminately to the whole class of solid hydrocarbons, which have, or have nearly the formula  $C_m H_m$ , the identity of which has been taken for granted, in the absence of any true knowledge as to the chemical nature of the substances from the decomposition of which by heat they are produced. The different melting-points however of these substances point out to us at once a distinction between them. The paraffin of M. LEWY melted at  $46^{\circ}8$ . A specimen of the paraffin of wood given to me by Professor LIEBIG, and which that gentleman received from REICHENBACH, its discoverer, melted at  $43^{\circ}5$  C.; ETTLING's paraffin at  $57^{\circ}$  to  $58^{\circ}$  C. I confess it is difficult for me to conceive what substance in a state approaching to purity LEWY analysed from the wax having the melting-point he has given, since nothing is easier than to raise the melting-point of the paraffin from the wax to  $56^{\circ}$  C., although beyond this any change is effected with difficulty.

Cerin alone gives on distillation hardly a trace of this hydrocarbon, while it forms a principal product of the distillation of myricin. The palmitic acid is separated by saponification, and the general preparation of the substance is the same as in the similar case of the ceroten from Chinese wax, to which substance it is closely analogous. If the hydrocarbon from the distillation of the pure myricin, the acids having been boiled out with potash, be pressed out in a press between blotting-paper, it will have a melting-point of about  $56^{\circ}$  C. This can be raised by further crystallization out of ether to  $60^{\circ}$  C. The analysis of the substance in this condition shows the presence of some body containing oxygen, in addition to the hydrocarbon.

	CO <sub>2</sub> .	HO.
0.2606 grm. of this substance gave . . . .	0.8094	0.3402
giving in 100 parts,—		
Carbon . . . . .	84.74	
Hydrogen . . . . .	14.51	
Oxygen . . . . .	0.75	
	100.00	

Another analysis gave similar results. This led me to prepare the substance in rather a different manner. The paraffin having been carefully pressed out in the manner described, was rectified over potassium, which destroys the oxygen compound. The distillate is perfectly white: it contains a little oil, which may again be pressed out. By crystallization out of pure ether, the melting-point may now be raised to  $62^{\circ}$  C. This substance was analysed.

	CO <sub>2</sub> .	HO.
0.261 grm. gave . . . .	0.8165	0.3393

giving in 100 parts,—

Carbon . . . . .	85·31
Hydrogen . . . . .	14·44
	<hr style="width: 50%; margin-left: auto; margin-right: 0;"/>
	99·75

The formula  $C_m H_m$  demands—

$C_m$ . . . . .	85·71
$H_m$ . . . . .	14·28
	<hr style="width: 50%; margin-left: auto; margin-right: 0;"/>
	99·99

The difference between the hydrogen calculated and found is only 0·16 per cent., which is as near to theory as such analyses can be expected to come. Cerotin melts at 81° C. The hydrocarbon I have called ceroten melts at 57° to 58°. Melissin melts at 85°. The wax hydrocarbon at 62° C., showing a precisely analogous difference in their melting-points. Owing to the numerous operations which are necessary before this hydrocarbon can be procured in a pure state, I have been unable to make further experiments with the pure substance. The analyses, however, the analogy of this other substance and the mode of its formation, can leave no doubt but that it is the hydrocarbon of the wax-alcohol  $C_{60} H_{60}$ , to which may be given the name of melen.

*The Nature of Myricin.*

The analogy of the products of the decomposition of myricin by alkalies and by heat, to those of the Chinese wax and of spermaceti under similar circumstances, would lead us to suspect that a similar relation exists between the substances to which these products are due. If, however, we take the numbers which have been obtained by analysis for this body, those for example of ETTLING\*, or those of LEWY†, and attempt from these to reckon out a formula which shall give a rational account of these decompositions, we find a considerable deficiency of carbon. I give one of LEWY's analyses, with which other analyses of himself and other chemists are sufficiently accordant‡.

Carbon . . . . .	80·28
Hydrogen . . . . .	13·34
Oxygen . . . . .	6·38
	<hr style="width: 50%; margin-left: auto; margin-right: 0;"/>
	100·00

The formula  $C_{92} H_{92} O_4$ , which would account in a simple manner for the decompositions,—

$C_{32} H_{31} O_3$	$C_{32} H_{32} O_4$
$C_{60} H_{61} O$	$C_{60} H_{60}$
<hr style="width: 50%; margin-left: auto; margin-right: 0;"/>	<hr style="width: 50%; margin-left: auto; margin-right: 0;"/>
$C_{92} H_{92} O_4$	$C_{92} H_{92} O_4$

\* LIEBIG'S Annalen, ii. 267.

† Annales de Chimie, xiii. 443.

‡ Ibid.

requires—

	Atomic weight.
C <sub>92</sub> . . . . 81·65	552
H <sub>92</sub> . . . . 13·60	92
O <sub>4</sub> . . . . 14·75	32
100·00	676

leaving a difference of one and a half per cent. of carbon, a difference too great to be attributed to any accidental error.

I have stated that the decompositions of the myricin are far from being so simple as those of the Chinese wax, and that in order to obtain either the acid or the wax alcohol, long and repeated crystallizations are necessary. This at once led me to the suspicion that the so-called myricin was no pure chemical substance, but a mixture of two or more bodies. Subsequent experiment confirmed this view.

The residue of the wax, after the cerotic acid has been boiled out by alcohol, melts at 64° C. It is but very slightly soluble in alcohol. Pure ether, however, will dissolve it without much difficulty. It crystallizes out of this reagent in light feathery crystals. The precipitate and the residue from the solution, evaporated to dryness, have different melting-points. I succeeded in this manner in raising the melting-point of the precipitate to 71°·5. This end may be more readily obtained by adding a small quantity of naphtha to the ether.

The following analyses were made of a substance of 72°, which after repeated crystallizations was precipitated on the filter out of the hot solution, the filter being kept hot by means of a hot water apparatus. I have not succeeded in raising the melting-point beyond 72°. The substance is now highly crystalline in appearance, which the impure myricin is not, and of about the consistency of wax. I regard it in this state as pure.

	CO <sub>2</sub> .	HO.
I*. 0·2592 grm. of substance gave . . . .	0·7735	0·3135
II. 0·2243 grm. of substance gave . . . .	0·672	0·269

which give in 100 parts,—

	I.	II.
Carbon . . . .	81·38	81·70
Hydrogen . . . .	13·44	13·33
Oxygen . . . .	5·18	4·97
100·00	100·00	100·00

These numbers are very different from any which have been before obtained for any substance from the myricin, and different from those which I myself have ob-

\* The thorough combustion of these waxes is difficult, and I have made many experiments to ascertain the best method of analysis. Bichromate of lead was the material generally employed. But when the combustion is made very slowly, I believe it to be complete even with oxide of copper alone. The greater number of such analyses in this investigation were made by my chemical assistant, Mr. L. HOFFMANN, to whose care and skill I am much indebted.

tained for substances of a lower melting-point. The crystalline appearance marks the purity of the substance, and notwithstanding the slight difference in the hydrogen, I cannot but regard it as the body  $C_{92}H_{92}O_4$ , with the calculated formula of which, as given above, it sufficiently agrees. I must add that the substance is separable with extreme difficulty. The next precipitate from the solution from which the above substance had been separated, had a melting-point half a degree lower, and gave to analysis rather less carbon, namely, C. 81.0 per cent.

The greater part of the difficultly saponifiable portion of the wax appears to consist of the substance the analysis of which I have just given, and to which we may confine the name myricin. We have, however, clearly some other body present accompanying it, the products of the decomposition of which by potash are to be found with both the acid and the wax-alcohol procured by saponification of the impure substance, which, as I have said, render extremely difficult the preparation of these bodies in a pure state. I shall proceed to give some experiments which throw some true light upon the nature of this substance, although I cannot say that its history is satisfactorily made out. The solution of ether or naphtha (p. 278) from which the melissin of  $85^\circ$  has been separated, still contains a large quantity of substance of a similar appearance, but of a melting-point much lower than that of the melissin itself. Notwithstanding however the differences in the melting-point, analysis shows us but little or rather no difference in the constitution of the different portions of this substance. In the case for example of a substance melting at  $78^\circ.5$  C.,—

	CO <sub>2</sub> .	HO.
0.2522 grm. gave . . . .	0.764	0.324

which gives in 100 parts,—

Carbon . . . . .	82.59
Hydrogen . . . . .	14.27
Oxygen . . . . .	3.14
	100.00

In the case again of a substance melting at  $72^\circ$ ,—

	CO <sub>2</sub> .	HO.
0.249 grm. gave . . . .	0.75075	0.317

which gives in 100 parts,—

Carbon . . . . .	82.22
Hydrogen . . . . .	14.14
Oxygen . . . . .	3.64
	100.00

Other analyses gave similar results.

These analyses do not differ seriously from one another, and give precisely the numbers of the melissin itself (p. 279). The numbers however are consistent with various formulæ besides that of the melissin. At 72° the melting-point is extremely constant. A portion of substance was obtained at this melting-point by repeatedly filtering the ethereal solution from the melissin which first crystallized out of the hot liquid. A time arrived when there was no difference between the melting-point of the portion which first crystallized out of the hot solution and which was on the filter, and that which afterwards crystallized out of the fluid which had passed through. The melting-point in both cases was 72°. By heating with lime and potash, as in the case of melissin, this substance of 72° also affords an acid, which after the usual preparation, gives very different numbers to those of the melissic acid. This acid melts at 77°·5.

	CO <sub>2</sub> .	HO.
I. 0·256 grm. gave . . . . .	0·735	0·3015
II. 0·267 grm. gave . . . . .	0·765	0·311
III. 0·2551 grm. gave . . . . .	0·730	0·2995

giving in 100 parts,—

	I.	II.	III.
Carbon . . . . .	78·28	78·14	78·05
Hydrogen . . . . .	13·09	12·94	13·05
Oxygen . . . . .	8·63	8·92	8·90
	<hr/> 100·00	<hr/> 100·00	<hr/> 100·00

Between the second and third analyses the substance was twice crystallized out of ether. The substance dissolved by the ether had the same melting-point of 78° as the substance on the filter.

The silver salt of this acid gave the following numbers :—

	CO <sub>2</sub> .	HO.
I. 0·5054 grm. of substance gave . . . . .	1·127	0·4572
II. 0·5182 grm. of substance gave . . . . .	1·1505	0·467

giving in 100 parts,—

	I.	II.
Carbon . . . . .	60·80	60·56
Hydrogen . . . . .	10·05	10·01
Oxygen and silver . . . . .	29·15	29·43
	<hr/> 100·00	<hr/> 100·00

I. 0·617 grm. gave on ignition . . . . . 0·1375 silver.

II. 0·7315 grm. gave on ignition . . . . . 0·1625 silver.

giving per cent.—

	I.	II.
Silver . . . . .	22·28	22·21

These analyses perfectly agree with the formulæ for the acid,  $C_{49}H_{49}O_4$ .

	Calculated.
$C_{49}$ . . . . .	78·4
$H_{49}$ . . . . .	13·0
$O_4$ . . . . .	8·6
	<hr/>
	100·0

	Calculated.
$C_{49}$ . . . . .	60·9
$H_{48}$ . . . . .	9·9
$O_4$ . . . . .	6·8
Ag. . . . .	22·4
	<hr/>
	100·0

If we compare the numbers of this acid with those of the substance from the oxidation of which it was derived, we shall see that it is impossible to account for the changes in the same simple manner as in other cases of such transformation. It would not be difficult to reckon out a formula that without great violence should account for it, but it is hardly worth while to do so, since notwithstanding the perfect agreement of the calculated and theoretical numbers, it is impossible to assert with certainty that either it or the body from which it is derived are pure chemical substances. There is too great a difficulty in the perfect separation of the melissin to lead us to hope that it can absolutely be removed by the method I have given. I failed in attempting to procure in larger quantities this substance of  $72^\circ$ . The melting-point was very constant at  $75^\circ$ , but on oxidizing a considerable quantity of this substance with lime and potash, acids were procured, which by crystallization were separable in the same manner as the substance from which they were derived, and the purification and perfect separation of which presented the same difficulties. I obtained in this way an acid having nearly the melting-point of  $85^\circ$ , the melting-point of melissic acid, and also an acid with a lower melting-point than  $77^\circ$ , but of which the melting-point was not so absolutely constant as to induce me to investigate it further. I give however these analyses, since they unquestionably prove the existence of some other body in addition to the melissin, in the products of the saponification of wax, which by oxidation is capable of passing into an acid belonging to the series  $C_m H_m O_4$ . Since it is only a pure body or a mixture of acids of this series which could give rise to the results I have given, and from the great difficulty of separation, the acid in all probability contains a very large number of equivalents of carbon, whether it have precisely the formula I have above given or not.

Mixed with the palmitic acid of  $62^\circ$ , is found another acid of a much lower melting-point, and which presents similar difficulties of separation from the palmitic acid to those of the substance mixed with the melissin from the melissin itself. This acid is very soluble in alcohol, unctuous to the touch, and of a very low melting-point. I do not, however, mean to assert that the other wax-alcohol exists in the wax in

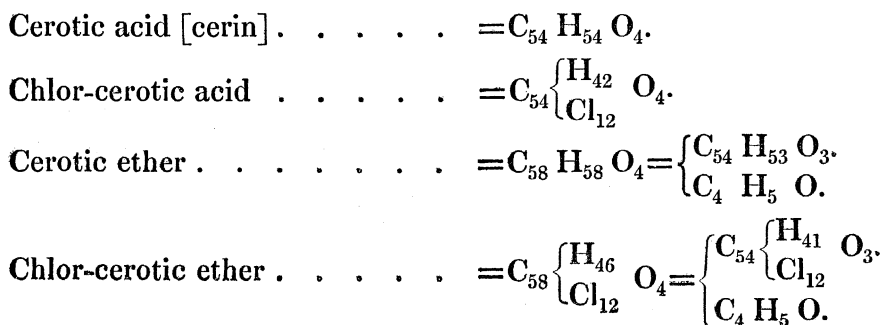
combination with this unctuous acid, the presence of which is very probably due to another source.

This alcohol may possibly, as well as the melissin, be combined with palmitic acid, or it may be in some altogether different form in the wax. Even after long boiling with alcohol, the myricin has a slight wax smell, and it is possible that this unctuous acid is the product of the action of potash upon the oil which is one of the constituents of the wax, and from which I have in fact procured an acid of this nature. This oil, or rather grease, which was analysed by LEWY, is a very curious substance. The other constituents of the wax are, in a pure state, inodorous and crystalline, and to it the wax owes its tenacity and peculiar smell. I have made some experiments as to its nature, and procured from it also an acid and an unsaponifiable substance; I will not, however, here enter upon the matter, hoping at some future time to resume its investigation.

I must not omit to mention, with reference to the bees'-wax from Ceylon, of which I spoke in a former paper, and which contained no cerotic acid, that it possesses all the general characters of the other portion of the wax. Like the impure myricin, it contains more than one substance. The wax itself has a melting-point of  $65^{\circ}5$ . When digested with ether in the cold, a portion is taken up by the ether, and a residue left of the melting-point of  $67^{\circ}$ ; and, when dissolved in ether, if the ethereal solution be filtered while warm from the first portions of the precipitate which crystallizes out, a substance may be obtained, of the melting-point of  $72^{\circ}$ , crystalline in appearance, hardly at all acted on by a solution of potash, but readily saponified by melted potash; resembling in short in all its properties the pure myricin. The products of the saponification of the wax itself closely resemble those of the impure myricin, and present similar difficulties of separation.

An acid may be obtained from it having the character of palmitic acid, and I have also procured from this wax the substance melissin, having a melting-point of  $84^{\circ}$ . The analysis VI. p. 279, was made from a preparation from Ceylon wax.

I will sum up the results of this investigation by giving a list of the principal substances of which an account has been given in this and the preceding papers. This table will exhibit, at one view, their relations to one another, and to the natural substances from the decomposition of which they are derived.





Cerotin . . . . .	=	$C_{54} H_{56} O_2$ .
Sulphate of oxide of cerotyle . . . . .	=	$SO_3, C_{54} H_{55} O + HO$ .
Chlor-cerotal . . . . .	=	$C_{54} \left\{ \begin{array}{l} H_{41} \\ Cl_{13} \end{array} \right. O_2$ .
Ceroten [paraffin] . . . . .	=	$C_{54} H_{54}$ .
Chlor-ceroten . . . . .	=	$\left\{ \begin{array}{l} C_{54} \left\{ \begin{array}{l} H_{35} \\ Cl_{19} \end{array} \right. \\ C_{54} \left\{ \begin{array}{l} H_{33} \\ Cl_{21} \end{array} \right. \\ C_{54} \left\{ \begin{array}{l} H_{32} \\ Cl_{22} \end{array} \right. \end{array} \right.$
Chinese wax . . . . .	=	$C_{108} H_{108} O_4 = \left\{ \begin{array}{l} C_{54} H_{53} O_3 \\ C_{54} H_{55} O \end{array} \right.$
<hr/>		
Melissin . . . . .	=	$C_{60} H_{62} O_2$ .
Chlor-melal . . . . .	=	$C_{60} \left\{ \begin{array}{l} H_{45.5} \\ Cl_{14.5} \end{array} \right. O_2$ .
Melissic acid . . . . .	=	$C_{60} H_{60} O_4$ .
Melen [paraffin]. . . . .	=	$C_{60} H_{60}$ .
Palmitic acid. . . . .	=	$C_{32} H_{32} O_4$ .
Myricin (pure) . . . . .	=	$C_{92} H_{92} O_4 = \left\{ \begin{array}{l} C_{32} H_{31} O_3 \\ C_{60} H_{61} O \end{array} \right.$

I might add to this list the acid  $C_{49} H_{49} O_4$ , the constitution of which however, for the reasons I have given, I cannot consider to be made out with sufficient certainty.

We should naturally suspect some intimate chemical relation between wax and fat from their similar appearance and properties. This suspicion gave rise to the idea that wax was convertible into fat, and to the hypothesis that wax was to be regarded as the aldehyde of stearic acid, and was capable of passing into that substance by a simple process of oxidation, a view of its chemical nature entirely without foundation. From the preceding inquiry, we arrive however at the knowledge of a no less remarkable relation between these substances.

Margaric acid was recently the last of that singular series of acids of the type  $C_m H_m O_4$ , which commencing with formic acid comprehended acetic acid, the volatile acids of butter and the acid of spermaceti, and æthal was the last of the corresponding alcohols. In the wax acids and alcohols of which an account has been given in this and the preceding papers, we have bodies at the other extremity of the series standing in a similar relation to margaric acid and to æthal, as that in which acetic and butyric acid, and alcohol and potatoe oil stand to them at the commencement.

An intervening acid of the series, the acid  $C_{44} H_{44} O_4$ , has lately been discovered by VÖLCKER\* in the oil of the *Guilandina Moringa*, and the investigation of the numerous class of vegetable oils and waxes will doubtless afford other bodies of the group.

Notwithstanding the many different properties of these substances, we find their chemical analogies constant, and the mutual relation of the acid, the alcohol and the hydrocarbon, is the same between bodies containing sixty as between those containing only four equivalents of carbon. Through at least half the series, from thirty to sixty equivalents, the same physical type of fat prevails. As a fat is doubtless but a soft kind of wax, so may not alcohol be but a very fluid form of fat? Alcohol has not yet been solidified, but one cannot help suspecting that when solidified it will appear as a wax or fat.

Direct experiment has shown us that in the body of the bee sugar is converted into wax. A simple analysis of the two substances showed that the carbon and hydrogen were in the same ratio in both, and that the change could be effected by a simple deoxidation of the sugar. Of the way in which this change is effected we are ignorant. The true formula of these wax substances however shows that they belong to the very type of bodies which are the ordinary products of fermentation, and are connected with them by the strongest chemical analogies. A new mode of fermentation produced butyric acid out of sugar; might not another kind of fermentation produce wax?

Until we know the nature of the whole of the ingredients of the wax, it is useless to speculate on the law of such a change. Although the wax itself is no pure chemical substance, but a mixture of substances differing nearly three per cent. from one another in their amount of carbon, yet the analysis of the whole bees'-wax gives results showing in different specimens which I have examined, no difference of constitution which analysis can reach. This renders it probable that the action is definite, and that the sugar in all cases loses the same amount of oxygen, although the remaining elements may in different cases be differently grouped.

\* LIEBIG'S Annalen, vol. lxiv. p. 342.