VII.—*On the Chemical Composition of Canaüba Wax.*

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THE wax-like coating which protects the leaves and fruits of many plants has received little attention at the hands of chemists, mainly probably because its quantity is small, and the difficulties of collecting it in many cases almost insuperable.

In Canaüba wax, however, commerce supplies us with a material directly derived from a plant which furnishes such a wax in appreciable quantities. This vegetable wax is the product of a palm, the *Copernicia cerifera* of botanists, the Canaüba tree of the Brazilians. It grows to a height of 20 to 40 feet, and when young its trunk is covered with leaves, which, however, in the older plants are found only at its summit in a globular cluster. Its sap yields an amylaceous food, its wood is a valuable timber, while its younger leaves furnish in the glaucous coating that protects them, the wax-like body, the chemical nature of which the following investigation may contribute to elucidate. The leaves are shaken, after being detached from the tree, and the wax which they yield, to the amount of some 50 grains per leaf, is melted into a mass.

In this state it is a pale yellow body, with a faint tinge of green, considerably harder at ordinary temperatures than beeswax, and from the descriptions of the wax made from the noble palm, the *Ceroxylon Andicola* of the Cordilleras, it would seem to be also harder and less resinous than this latter body.

The specific gravity of Canaüba wax is 0.99907, and its melting point is about 84° C. On being incinerated it yields 0.14 per cent. of ash, for the most part consisting of silica and iron with some sodic chloride.

Many trials were made as to the best way of breaking this body up into its constituent compounds. The following methods were those ultimately adopted for the purpose.

A quantity of the crude substance was boiled with alcoholic solution of potash containing one-sixth of its weight of alkali, till the liquid became clear, when the spirit was distilled off. The residue, in which are contained the saponified products,

was poured into a solution of neutral plumbic acetate, a yellow colour immediately developing itself throughout the mass. The whole was then carefully dried, powdered, and extracted with ether. Wax alcohols dissolve in this liquid in large quantities, and mere successive crystallisation will give one of them, which seems to be melissin, in great purity. The insoluble lead salt can afterwards be decomposed by hydric chloride. In another experiment 12 oz. of the wax were saponified with an alcoholic solution of potash, as already mentioned; as soon as the liquid was clear, it was precipitated by cold water, the alcohol was then distilled off, and from the mixed soap and alcohols, which dissolve in the boiling water, the acids were set free by hydric chloride. The mingled mass of acids and alcohols thus formed was then dissolved in boiling alcohol, and the acids were saturated with ammonia; the ammonia soap, produced by this means, was next thrown down by baric chloride. The alcohol was now distilled off, and the precipitate, after having been thoroughly extracted with boiling water, was thrown on a filter. This precipitate was dried, powdered, and extracted several times with spirit. The residue was reserved for an examination of the acids contained in it.

The part dissolved by alcohol was extracted with ether. Repeated crystallisations from this liquid yield at length a substance melting at first at 87° , but ultimately rising to 88° . In this state the substance, when fused on a watch-glass, exhibits as it cools the concentric undulating rings characteristic of cooled wax alcohols. In appearance it is a very hard, semi-transparent, electric body, exhibiting when in mass but little crystalline structure, soluble in hot alcohol and in ether, though not in large amount in either of these liquids. From its alcoholic solution it separates, on cooling, as a gelatinous mass. From ether, on the other hand, it separates in small foliated crystals. Its analysis produced the following numbers:—

- I. 0.2858 grm. gave 0.8632 grm. carbonic acid and 0.365 grm. water.
- II. 0.2914 grm. gave 0.8824 grm. carbonic acid and 0.3738 grm. water.
- III. 0.2942 grm. gave 0.8898 grm. carbonic acid and 0.3768 grm. water.

These results correspond to the following percentages:—

	I.	Experiment. II.	III.	Theory. (C ₃₁ H ₆₄ O).
Carbon	82·37	82·6	82·46	82·30
Hydrogen ..	14·21	14·28	14·24	14·16
Oxygen	—	—	—	3·54
				<hr/> 100·00

The alcohol, from these numbers, was assumed to be melissin. In order to determine its constitution with greater exactitude, the homologous acid resulting from its oxidation was formed. This was effected in the usual manner: the tube containing an intimate mixture of the alcohol and potash-lime was kept by means of an air-bath at a nearly constant temperature of 270°, this point being never exceeded. Pure hydrogen was evolved for some hours and, when this gas ceased to be developed, the substance in the tube was removed and the acids were separated by boiling with hydric chloride.

The eliminated acids were dissolved in alcohol, and their solution was filtered whilst hot; when cold, the alcohol was removed by filtration. The precipitated acid was again dissolved in a very large amount of cold alcohol, and then boiled, after which this alcoholic solution was converted into an ammonia soap, and precipitated with baric chloride. This barium salt was filtered off from the boiling liquid, and repeatedly exhausted of any unoxidized wax alcohol it might contain, with boiling ether, the process being continued till the ether dissolved no further trace of substance. The barium was then removed by boiling the pure salt with hydric chloride. Dissolved in hot alcohol, and filtered from the remains of undecomposed barium salt, the melissic acid, after recrystallisation, presented, on being fused and broken, a fracture of highly crystalline aspect; and a fragment fused on a watch-glass gave, on cooling, the needle-like crystalline radiations which mark the cooling of the wax acids.

This substance was found to be in a high degree electrical; it melted at 91°, and was only with the greatest difficulty at all soluble in alcohol. Its analysis gave the following results:—

I. 0·2981 grm. gave 0·872 grm. carbonic acid and 0·36 grm. water.

II. 0·2972 grm. gave 0·8666 grm. carbonic acid and 0·3621 grm. water.

III. 0.2842 grm. gave 0.8286 grm. carbonic acid and 0.3462 grm. water.

These numbers corresponding to a percentage composition of—

	Experiment.			Theory.	
	I.	II.	III.	($C_{31}H_{62}O_2$).	($C_{30}H_{60}O_2$).
Carbon	79.78	79.51	79.49	79.83	79.65
Hydrogen . . .	13.42	13.53	13.55	13.30	13.27
Oxygen. . . .	—	—	—	6.87	7.08
				<hr/> 100.00	<hr/> 100.00

The silver-salt of this acid was now prepared. An alcoholic solution of the acid, after saturation with ammonia in slight excess, was precipitated by an alcoholic solution of argentic nitrate, and the pure white precipitate filtered off and washed in the dark. Dried at 100° , it presented the appearance of a greyish-white powder, devoid of any waxy lustre, and very readily affected by the light. Its analysis gave the following results :—

I. 0.3692 grm. of the salt gave 0.8726 grm. of carbonic acid and 0.357 grm. of water.

II. 0.3276 grm. of the salt yielded 0.0632 grm. of silver.

III. 0.4192 grm. of the salt yielded 0.0816 grm. of silver.

These numbers correspond to the following percentage composition :—

	Experiment.			Theory.	
	I.	II.	III.	($C_{30}H_{59}AgO_2$)	($C_{31}H_{61}AgO_2$)
Carbon	64.46	—	—	64.4	64.92
Hydrogen..	10.75	—	—	10.55	10.65
Silver.	—	19.29	19.45	19.32	18.85
Oxygen. . . .	—	—	—	5.73	5.58
				<hr/> 100.00	<hr/> 100.00

In consequence of the large amount of alcohols yielded by the former process, I was convinced that these alcohols were present in the free state. To establish this, I endeavoured, in a fresh quantity, to separate them by direct crystallisation with alcohol, my preliminary experiments having proved the wax to be only partially soluble in that liquid. 400 grammes treated in this manner, after an enormous number and continuation of boilings, which at last barely removed a trace of substance, gave—

126 grammes of soluble ingredients, which melted at 81° ;

274 grammes of insoluble ingredients, which melted at 86° .

The *insoluble* portion, when saponified by potash, did not turn of so bright a yellow as the whole mass of wax does under the same treatment. This potash solution was then thrown down, as before, by a solution of lead, and the precipitated lead-salt again dried, pulverised, and exhausted with alcohol. That part of the lead-salt insoluble in spirit corresponded to 85 grammes of acids, which were liberated from it by hydric chloride. From the portion dissolved in alcohol that solvent was distilled off, and the dried mass treated with ether. The boiling ether dissolved a number of wax alcohols, and left a residuary lead-salt which corresponded to 30 grammes of acids. The ethereal solution, on cooling, deposited mixtures of alcohols, from which, as before, successive crystallisations yielded large amounts of melissin.

The *soluble* portion of this fresh quantity, weighing 126 grammes, though repeatedly crystallised first from alcohol and afterwards from ether, yielded no products that after fusion on a watch-glass would give any crystalline substance as they cooled. This appeared to be due to a resinous body which, though very soluble in these liquids, adhered pertinaciously to the alcohols as they separated out on cooling. With a view to saponifying and precipitating this substance, a minute amount of potash was added to the alcoholic solution, which instantly turned very yellow and of a much brighter colour than was observed on subjecting the insoluble ingredients of the wax to like treatment; plumbic acetate threw down a precipitate comparatively trifling in quantity; and on boiling it in alcohol, it was noticed that the bodies which dissolved in this liquid no longer gave any yellow colour with potash. The resinous body thus eliminated in the form of a lead-salt, was too small in amount and too readily decomposed to invite further enquiry.

The mass of substance, now dissolved in alcohol, began, after a single crystallisation, to exhibit, on cooling from fusion on a watch-glass, the concentrically annular ridges peculiar to the class of wax alcohols. The ridges were far less coarse than in the case of cerotin, and a few crystallisations from alcohol and ether yielded an individual alcohol of great purity, which crystallised at 86° , and was, in fact, melissin.

The existence in the free state of a wax alcohol in Canaüba

wax, to the amount of about one-third of its mass, is a fact in vegetable physiology of no little interest.

The melissin thus obtained is invariably accompanied by another body in very small relative proportions to it, which is deposited in the flasks in fine crystals; it does not yield annular surfaces on fusion, but exhibits a crystalline structure of an entirely different kind.

It is a circumstance important to remark, that the melissin is present in much larger proportion to the mass of the other alcohols in the part soluble in spirit than it is in the portion insoluble in this liquid.

The whole of the residuary alcohols, both from the free alcohols in the soluble and from the alcohol bases set free from the insoluble part of the wax, were, after the separation of the first crystallisations of the melissin, mixed and treated together. Dissolved in boiling alcohol and filtered when cold, these mixed substances fused at a variable melting point of from 81° to 86° , and did not give a clear liquid at any temperature. By several recrystallisations more melissin was extracted and a body obtained which had a melting point of 87° , but which neither solidified in annular concretions nor presented the silky crystals characteristic of melissin. After these had been separated, the residues began to melt at 81° , and only became clear at temperatures over 90° . On treating them with benzol, there crystallised out a body having a melting-point of 88° , which by repeated recrystallisation from this liquid could be raised to 96° . After it had been crystallised from ether a few times, its melting-point was further raised to 105° , and at this stage it solidified with crystalline characters similar to those of cerotic acid, but did not saponify with an aqueous solution of potash. The residues of the solvents, from which this body melting at 105° had separated, yielded at once a substance that melted quite clearly at 84° , whence it may be concluded, that they contained no compound with a higher point of fusion. Substances crystallising between 80° and 84° are separated by the solvents from which this last body was obtained, but they are devoid of crystalline structure.

Owing to the small amount of these substances obtained from even so large an amount of wax as 400 grammes, a much larger quantity of the Canaüba wax was next worked upon, and the residues from the various stages of the treatment of these

400 grammes were mixed with the corresponding substances furnished by the new material. Two pounds of the wax were treated with a mixture of ordinary benzol and alcohol, a liquid which, not to mention its greater solvent power, has its extractive influence enhanced by its higher boiling point. A result of the latter fact is that the wax fuses and is thus more readily acted upon by the solvent. Each portion, as before, was saponified by an alcoholic solution of potash.

The *insoluble* part was precipitated by plumbic acetate. By operating on small quantities at a time, and allowing the flask to stand until the lead salt had fallen, the melissin could be poured off in a state of partial precipitation from the solvent before the latter had become cold; or it may be allowed to cool, when the lead salt will be found clotted into a lump at the bottom of the flask, thus enabling the overlying portion containing the wax alcohols to be mechanically separated with great facility. The lead salt, of course, is in this way only partially freed from melissin; it contains, however, none of the substance which melts at 105°. By again treating the mass thus separated from the lead salts, with the same solvents, the melissin may be obtained in considerable purity; it still, however, contains some lead salt.

The *soluble* part was saponified by potash in quantities of about 6 oz. at a time. By filtering the liquid before it had become quite cold, the solution of the soap was separated from a quantity of very nearly pure melissin, which a few crystallisations rendered colourless and absolutely pure. The soap in the filtrate was precipitated by plumbic acetate, and in this way a little more melissin was obtained. It must here be remarked that the mixture of benzol and alcohol used in treating this last quantity of the wax, dissolved some of the compounds of melissic and other alcoholic bases with wax acids, and that therefore the precipitate produced by plumbic acetate in the soluble part contained a small quantity of lead salts and of acids which properly belong to the insoluble portion.

After all the melissin had been crystallised out, as far as could be, from both the soluble and the insoluble parts, their residues were mixed and treated as one. Solution in alcohol and repeated crystallisation added to the amount of melissin obtained. The residuary matter contained in the filtrates from these last quantities no longer exhibited annular crystallisation on a watch-

glass; they consisted, in fact, of a mixture of the substance melting at 105° , with a number of lower wax alcohols, whose chemical isolation is a problem for which at present there is perhaps no known satisfactory solution. In order to separate the body which melts at 105° , these residues were then dissolved in a very large quantity of alcohol, sufficient, in short, to retain, even when cold, the more soluble of the wax alcohols. When cold this liquid was filtered, and upon the filter there was left a substance which, though it began to melt at 84° , did not become transparent till it reached a temperature of 92° . Crystallisation from pure benzol rapidly brought its melting point to 97° , and, this degree attained, no amount of re-crystallisation could raise it above this temperature. With ether, however, as already mentioned, several crystallisations gave a body having a melting point of 105° , which cannot by any means be further raised, and this was, in fact, the substance previously described. Although the filtrates from the preparation of this compound yield, by a repetition of the process of crystallisation from ether, a further amount of it, this body is present in but very small proportions in Canaüba wax. Enough, however, was at last obtained for examination and analysis. It crystallises from its ethereal solution in little bosses or lumps, radiating from a centre. Fused on glass it solidifies with crystalline characters, unlike, however, those of wax alcohols; and it is far less electric than melissin. Its analysis furnished the following results:—

I. 0.271 grm. of the substance gave 0.778 grm. of carbonic acid and 0.3352 grm. of water.

These numbers correspond to the subjoined percentages:—

	Experiment.	Theory.
	I.	($C_{39}H_{32}O_3$)
Carbon	78.3	78.30
Hydrogen	13.73	13.71
Oxygen	—	7.99
		<hr/> 100.00

It is very difficult, however, to assign a formula to this anomalous substance, in the absence of more experiments as to its nature.

The filtrates from which the above body had crystallised,

yielded a series of substances melting respectively at 90° to 91° , 92° , and 95° ; these, however, were obviously mixtures.

The alcoholic bodies dissolved by the large amount of alcohol were next treated, with a view to a separation of the wax alcohols that they contain.

The benzol residues from which the substance melting at 105° had been procured were distilled to remove the benzol, and a considerable quantity of the spirit of the alcoholic solution of the lower wax alcohols was likewise driven off; these two residues were then mixed. On cooling, a large mass of mixed bodies was deposited, which were filtered off. This precipitate, of a dark colour, was then boiled with alcohol and animal charcoal, filtered once more whilst hot, and the spirit removed by distillation. By repeatedly crystallising this purified residue from ether, several bodies of the nature of wax alcohols were obtained; they were, however, necessarily in a state of only approximate isolation. Their melting points were more or less definite, being 72° , 73° , 75° , 78° , 80° 81° to 82° , 83° , and (a little melissin) 85° . There was, moreover, a small quantity of a substance melting at 84° , very similar to one melting at 78° ; this, however, was not melissin, and though cooling from fusion with highly crystalline characters, did not exhibit the annular kind of crystallisation. The alcohol melting at 78° appears to be that present in largest quantity, and is probably cerotin. The remainder of the above series were present in small, but pretty equal quantities. Sufficient of the alcohol which melts at 78° was obtained for the following analysis:—

I. 0.2722 grm. of the substance gave 0.809 grm. of carbonic acid and 0.3428 grm. of water.

These results correspond to the following percentage composition:—

	Experiment.	Theory.
	I.	($C_{23}H_{46}O$.)
Carbon	81.04	81.17
Hydrogen	13.99	14.12
Oxygen	—	4.71
		<hr/> 100.00

It may here be mentioned, that every attempt to obtain acids from these alcoholic bodies, by submitting them to the action of soda-lime, proved unsuccessful, from the fact of the lower acids

undergoing decomposition at the temperature necessary for the reaction with the higher ones.

In the endeavour to determine with greater exactness the nature of the alcohol, the iodide of its radical was formed. In the first instance this body was produced by the action of phosphorus and iodine, warmed gradually, and subsequently treated by boiling with water and a little sodic carbonate. The resulting substance was dissolved in benzol, and crystallised in large granular crystals. A similar preparation boiled with a strong solution of sodic carbonate gave a body with a melting point of 67° .

Subsequently the alcohol was treated by Von Fridau's method;* it was fused at a temperature of 120° to 135° C. in a sulphuric acid bath, a small quantity of phosphorus being dissolved in it, and iodine then added in excess. After being retained for some time at a temperature of 130° C., the mass was washed out with cold water, fused and shaken with water at 80° C. It was then dried and digested with ether, which left it with a melting point of 67° , having dissolved a body that separates from it with a fusing point of 70° to $70^{\circ}5$.

The comportment of the iodide with argentic oxide was then observed. A quantity heated with this oxide and a little water in a sulphuric acid bath to a temperature of 100° to 120° C. was converted into a pasty mass, which when dried and boiled with alcohol, was found to be soluble in this menstruum. As the solution cooled, an abundant deposit was formed of a body, the fusing point of which was found to be 67° . Hence it appears that this reagent does not act upon the iodide.

Analysis of the iodide produced by the above methods gave the following results:—

I. 0.249 grm. of iodide, prepared by means of phosphoric iodide, when burnt with plumbic chromate in a current of air, gave 0.2493 grm. water and 0.5946 of carbonic acid. A residue of unburnt carbon weighing 0.0015 grm. remained in the platinum boat.

II. 0.1009 grm. of the same preparation, when heated with lime and sodic carbonate, gave 0.0406 grm. of argentic iodide. The smallness of the quantity employed magnifies the error of analysis.

III. 0.2085 grm. of iodide, prepared by Von Fridau's method,

* Liebig's Handwörterbuch, Bd. II, 924.

gave, when burnt, 0·2095 grm. of water, and 0·4902 grm. of carbonic acid. A residue of unburnt carbon weighing 0·0009 grm. remained in the platinum boat.

These numbers correspond with the following percentage composition :—

	Experiment.			Theory.	
	I.	II.	III.	(C ₃₀ H ₆₁ L.)	(C ₃₁ H ₆₃ L.)
Carbon	65·722	—	64·556	65·693	66·193
Hydrogen..	11·121	—	11·16	11·132	11·209
Iodine	—	21·744	—	23·175	22·598
				<hr/> 100·000	<hr/> 100·000

The behaviour of the iodide with ammonia and aniline was next examined. When dry ammonia was passed through the fused iodide at 150° to 160° C., it soon became turbid, and after the lapse of some time a white granular precipitate was formed in the fused mass. Heated with strong aqueous ammonia in sealed tubes, it invariably became opaque, and on breaking the points of these tubes under water they immediately filled. The compound resulting from each experiment, when boiled with water, evolved much ammonia, and had then a melting point of 68°·5 to 69° C., indicating a return to the state of simple iodide. This body, moreover, appeared to decompose spontaneously.

On boiling some of the iodide with aniline, and allowing the solution to cool, a precipitate formed. This was washed with cold ether, in which it is almost insoluble, and then boiled in this liquid, which dissolved it with great ease, and deposited it again in fine crystals. The product, when fused, evolved aniline, leaving a residue with a melting point of 68° to 69°.

The preparation of a corresponding chloride of the alcohol radical was next attempted. A quantity of melissin, after repeated treatment with phosphoric pentachloride, yielded a compound with a melting point of about 65°, which, however, sank to about 61° after warming the body with water. Boiling alcohol extracted from the above product a substance which fused at 64°·5, but after two crystallisations from ether was observed to melt at 65° to 65°·5. Two analyses of this substance gave the following results :—

I. 0·2201 grm. burnt in oxygen gave 0·2568 grm. of water, and 0·6035 grm. of carbonic acid.

II. 0.2154 grm. of a specimen, once more crystallised from ether, gave 0.246 grm. of water, and 0.5913 grm. of carbonic acid.

These numbers correspond with the following percentage composition:—

	Experiment.		Theory.	
	I.	II.	(C ₃₀ H ₆₁ Cl.)	(C ₃₁ H ₆₃ Cl.)
Carbon.....	74.784	74.865	78.861	79.065
Hydrogen ..	12.962	12.684	13.362	13.390
Chlorine	—	—	7.777	7.545
			<hr/> 100.000	<hr/> 100.000

These closely agreeing numbers at first suggested that a chlorine replacement had taken place, or that a bi-chloride of the biatomic radical had been formed; an inspection of their composition, however, renders this scarcely probable.

	C ₃₀ H ₆₀ Cl ₂ .	C ₃₁ H ₆₂ Cl ₂ .
Carbon.....	73.32	73.66
Hydrogen ..	12.22	12.27
Chlorine	14.46	14.06
	<hr/> 100.00	<hr/> 100.00

The body was therefore probably a mixture, a view which the change of melting point after treatment with water might be considered to confirm.

The acid produced by the action of sulphuric acid on melissin was also prepared, and its potash salt submitted to analysis. For this purpose the wax alcohol was heated with sulphuric acid in a water-bath, and continually pressed against the sides of the tube in which the operation was conducted, until it became completely dissolved, or rather perhaps suspended; by careful heating, merely a trace of discoloration is noticed. If, however, the temperature of the sulphuric acid be raised too high, and the wax be not stirred, the liquid soon becomes black, and much sulphurous acid is evolved. The wax, therefore, should never enter into more than incipient fusion. When taken up by the acid, it was dissolved in alcohol and saturated with alcoholic potash, which threw down a large white precipitate. Boiled repeatedly with water, this precipitate left a large flocculent residue, which when washed free from all sulphuric acid, was dried and examined. It was scarcely soluble in alcohol or ether,

and consecutive portions of these solvents removed about an equal amount, pointing to a slight solubility of the substance, and not an impurity of melissin. The purified body, thus obtained, fused at 96°. An analysis gave the following results:—

I. 0.165 grm., when burnt, gave 0.1681 grm. of water, and 0.3975 grm. of carbonic acid, and left in the platinum boat, a residue of sulphate of potash which amounted to 0.0249 grm.

These numbers correspond with the following percentage compositions:—

	Experiment.	Theory. (C ₃₀ H ₆₁ KSO ₄)	(C ₃₁ H ₆₃ KSO ₄)
Carbon.	65.69	64.75	65.26
Hydrogen ..	11.27	10.97	11.05
Potassium ..	6.74	7.01	6.84
SO ₄	—	17.27	16.85
		<hr/> 100.00	<hr/> 100.00

The above analysis, like many of the earlier mentioned ones of the alcohol and its acid, points to the formula C₃₁H₆₃KSO₄, unless the trifling amount of blackening at its first formation may have caused an increase of carbon and hydrogen in the body.

The examination of the acids combined in the Canaüba wax, with the alcohol bases, remains to be completed.

The pertinacity with which a resinous body adheres to these acids, and refuses to be separated from them by any amount either of crystallisation from solvents or of partial precipitation by any one or by different salts, suggested the cautious use of a high temperature. By gradually raising the temperature to about 240° in an air-bath, the resinous substance was successfully grappled with, and acids obtained by crystallisation from alcohol and ether, which, on fusion and cooling, came to present the characteristic features of wax acids on a watch-glass. Acids with melting points from 90°.5 and 130°—78° to 40°, were thus obtained, but their further isolation and examination remains to be worked out.*

* The greater part of the investigation, of which this memoir is an account, was carried out by the author in the years 1855-7; other duties then interfered and have since prevented its completion. It is published now, because, no one having taken up the subject exhaustively in the interval, the author trusts the interest attached to the composition of Canaüba wax may induce some other chemist to complete its chemical history.