XXXVI. Chemical examination of palm oil and cacao butter

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This gives the formula

Carbon	35	=	2675·225
Hydrogen	56	=	349·426
Oxygen	1	=	100·000
<hr/>			
3124·651.			

It is somewhat singular that this is precisely the composition which Dr. Kane found for the oil of *Mentha viridis*.

XXXVI. *Chemical Examination of Palm Oil and Cacao Butter.* By JOHN STENHOUSE, Esq.*

Palm Oil.

THIS oil has of late years become rather an important article of commerce, from the great extent to which it is employed in the manufacture of soap. It is chiefly imported from the coast of Africa, and is derived, according to some botanists, from the *Cocos Butyracea*, according to others from the *Avoira Elais*. It is extracted by boiling the bruised fruit in water; the oil collects as a cake on the surface, from which it is easily removed. It has a butyraceous consistence, is of a reddish yellow colour, and has an agreeable aromatic odour. When long kept it becomes readily rancid, and whitens at the same time, especially if exposed to the influence of the light and air. Soap made with the unbleached oil is of a yellow colour, but white soap may be made from it if the oil has been previously bleached. This may be done in various ways; by melting the oil in hot water and treating it with peroxide of manganese and sulphuric acid, or by keeping it melted, spread out in thin layers on iron plates. It has also been proposed to bleach it with hypochlorite of lime and dilute sulphuric acid; and bichromate of potash and muriatic acid have more recently been employed for the same purpose.

It was first observed by Zier, and the observation has been since confirmed by Messrs. Pelouze and Boudet, that palm oil is strongly acid, and that its acidity increases with the age of the oil. The quantity of free acid it contains is very great, often amounting to nearly a third of its weight. It is owing to this circumstance that palm oil is so remarkably easily saponifiable. Indeed, a very tolerable soap may be made from it by boiling it for a short time with the alkaline carbonates. Soap made from palm oil and soda is of a firm consistence, has an aromatic odour, and forms an excellent and agreeable detergent. The

* Communicated by the Author.

greater portion of the common brown soap made in Great Britain contains no tallow at all, but consists of a mixture of palm oil and common resin. The melting point of the specimen of palm oil I examined was 99° Fahr. It appeared to be pretty old. Palm oil was formerly supposed to contain margaric and oleic acids; but Mr. Fremy has lately subjected it to examination, and found it to contain a new acid, to which he has given the name of the palmitic. I am happy in being able to confirm the truth of his observations.

The mode of proceeding to examine the constituents of palm oil is to saponify it with caustic potash or soda, and then to decompose the soap with muriatic or tartaric acid. The mixture of palmitic and oleic acids thus obtained, is to be dissolved in boiling spirits of wine, in which it is very soluble, and allowed to crystallize. The crystals are to be collected and strongly pressed between folds of blotting paper, and again dissolved in alcohol. These operations are to be repeated eight or nine times till the palmitic acid crystallizes quite free from the oleic acid, which remains dissolved in the mother liquors. Before being subjected to analysis it was once more saponified, and the soap decomposed by muriatic acid. The palmitic acid had then a melting point of 140° Fahr. The following are the results of its analyses.

gramme.

I.	0.3025	gave	0.827	carbonic acid, and	0.338	water.
II.	0.3147	„	0.860	„	0.3545	„
III.	0.2950	„	0.8076	„	0.3305	„
IV.	0.2662	„	0.7262	„	0.3007	„

This is per cent.

	I.	II.	III.	IV.
Carbon ...	75.48	75.56	75.69	75.46
Hydrogen	12.41	12.51	12.48	12.51
Oxygen. . .	12.11	11.93	11.83	11.83
	<hr/>	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00	100.00

In order to determine the atomic weight of the acid the silver salt was prepared by precipitating an alcoholic solution of the soda soap with nitrate of silver.

gramme.

Oxide of silver.

I.	0.4992	salt gave	0.1456	silver =	31.31	p. cent. oxide.
II.	0.8204	„	0.2414	„	31.59	„
III.	0.6228	„	0.183	„	31.55	„
IV.	0.5375	„	0.1585	„	31.43	„
V.	0.5385	„	0.1575	„	31.41	„

Combustion with oxide of copper gave the following results:

I. 0·3205 salt gave 0·621 carbonic acid and 0·249 water.

II. 0·3305 „ „ 0·6395 „ „ 0·257 „

III. 0·2885 „ „ 0·559 „ „ 0·222 „

	I.	II.	III.
Carbon	53·57	53·50	53·58
Hydrogen.....	8·63	8·64	8·54
Oxygen.....	6·35	6·41	6·43
Oxide of silver...	31·45	31·45	31·45
	<hr/>	<hr/>	<hr/>
	100·00	100·00	100·00

The analyses of the hydrate agree best with the following formula :

		Per cent.
66 atoms of Carbon	5044	75·67
128 „ Hydrogen ..	824	12·33
8 „ Oxygen	800	12·00
	<hr/>	<hr/>
	6668	100·00

From the determination of the quantity of oxide of silver in the silver salt, however, I am disposed to prefer Mr. Fremy's formula for the hydrate as the more probable. It is

		Per cent.
32 atoms of Carbon	2446	75·37
64 „ Hydrogen...	399	12·40
4 „ Oxygen.....	400	12·23
	<hr/>	<hr/>
	3245	100·00

The formula $C_{32}H_{62}O_3 + AgO$ gives the following numbers for the silver salt :

		Per cent.
32 atoms of Carbon.....	2446	53·35
62 „ Hydrogen.....	387	8·44
3 „ Oxygen.....	300	6·54
1 „ Oxide of silver	1452	31·67
	<hr/>	<hr/>
	4585	100·00

The hypothetical composition of the anhydrous acid is consequently as follows :

		Per cent.
32 atoms of Carbon.....	2446	78·08
62 „ Hydrogen..	387	12·35
3 „ Oxygen	300	9·57
	<hr/>	<hr/>
	3133	100·00

The number 3133 agrees very nearly with the mean of five determinations of the silver salt, which gave 3165 for the

atomic weight of the anhydrous acid. The baryta salt was prepared in the usual way by precipitating an alcoholic solution of the soda soap with chloride of barium.

- Per cent. baryta.
- I. 0.5080 salt gave 0.150 carb. of baryta = 22.90
 II. 0.4947 „ „ 0.1462 „ „ = 22.92

The calculated quantity is 23.39 per cent. baryta. The atomic weight 3221, which this gives for the anhydrous acid, does not differ essentially from that found by the silver salt.

The following is the mode of preparing Palmitin, the compound of palmitic acid and glycerine. Palm oil is to be subjected to pressure between folds of linen, to separate the more fluid portion. The solid part is to be treated six or seven times with boiling spirits of wine to remove the palmitic and oleic acids, which are very soluble in that liquid. Palmitin, which, on the contrary, is nearly insoluble in hot spirits of wine, is to be then dissolved in hot æther and filtered, to separate it from the impurities which accompany it, and which remain on the filter. On the cooling of the solution the palmitin is deposited in very small crystals. These are to be pressed between folds of blotting-paper and recrystallized out of æther. These operations are to be repeated six or seven times till the palmitin is free from every trace of olein. It is then to be kept melted on the water-bath till the æther is driven off. Pure palmitin melts at 120° Fahr., and when saponified yields palmitic acid with the ordinary melting point of 140° Fahr. Palmitin is quite neutral; on being melted and not allowed to cool it does not crystallize, but forms a half transparent mass like white wax, but which differs from wax in being easily reducible to powder. It is almost insoluble in ordinary spirits; but absolute alcohol dissolves a little of it at a boiling temperature, which precipitates in white flocks on the cooling of the liquid. It is soluble in æther in every proportion. In its appearance and properties generally it very much resembles stearin; palm oil contains only a few parts per cent. of palmitin.

The following are the results of its analysis.

- I. 0.3235 gave 0.896 carbonic acid, and 0.3485 water.
 II. 0.3384 „ 0.9397 „ „ 0.3744 „
 III. 0.3317 „ 0.9195 „ „ 0.3665 „

or per cent.

	I.	II.	III.
Carbon	76.58	76.78	76.65
Hydrogen	11.99	12.29	12.27
Oxygen	11.43	10.93	11.08
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

The calculated numbers are,

35 atoms of Carbon	2675	76·73
66 „ Hydrogen ...	412	11·80
4 „ Oxygen	400	11·47
	<hr/>	<hr/>
	3487	100·00

and consequently palmitin must be regarded as consisting of

1 atom of Palmitic Acid =	$C_{32} H_{62} O_3$
1 „ Glycerine =	$C_3 H_4 O$
1 atom of Palmitin =	$C_{35} H_{66} O_4$

It is evident that this gives a very different formula for glycerine from the ordinary one, $C_6 H_{14} O_5$. This, however, gives a much simpler view of its constitution, proving it to belong to the class of simple organic oxides, like those of ethule and methule. This formula also affords a very simple explanation of the decomposition which glycerine undergoes when treated with peroxide of manganese and sulphuric acid. It is then, as is well known, converted into formic and carbonic acids, as under :

Palmitin when distilled gave acrolein, but no sebatic acid; palm oil, on the contrary, when subjected to distillation, yielded sebatic acid in abundance. This shows that the other acid which palm oil contains is the oleic, as it is the only fat acid known to yield sebatic acid by distillation.

Messrs. Pelouze and Boudet discovered that palm oil contains free glycerine, which can be obtained from it by treating the oil with hot water and filtering. I have also succeeded in obtaining it by this process. The acid which accompanied it was neutralized with carbonate of soda, and the glycerine extracted by alcohol. Its quantity was very inconsiderable. The presence of free glycerine in palm oil is what might have been expected from its containing so large a quantity of free palmitic and oleic acids.

Palm oil also contains small quantities of a blueish-green colouring matter. It is heavier than the oil, and forms a thinnish layer, which adheres to the lower part of the cake which palm oil forms when it is melted in water and allowed to cool; I thought at first it was owing to the palm oil having been prepared in copper vessels, but on examination I found that it was wholly of a vegetable nature. Hydrosulphate of ammonia had no effect upon it; caustic alkalies rendered it colourless; muriatic and nitric acid had a similar effect, but sulphuric acid blackened and apparently charred it.

Butter of Cacao.—Cacao butter is obtained from chocolate beans, the fruit of the *Theobroma Cacao*; either by subjecting the bruised beans to pressure between hot iron plates, or by boiling them in water and scumming off the oil as it collects on the surface. One pound of beans usually yields from three to four ounces of the oil. When first prepared it has usually a yellowish colour, but this can be easily removed by boiling it with water, or still more completely by treating it with hot alcohol. The taste of cacao butter is mild and agreeable; and its smell, which resembles that of the beans, is owing to the presence of an oily matter, which may be easily removed by one or two digestions with alcohol. With caustic soda cacao butter forms an excellent soap; but it is by no means very easily saponified. The melting point of cacao butter is stated by most chemical authors at 122° Fahr. I found that of the specimen I examined only 86° Fahr. MM. Pelouze and Boudet state it at 85° Fahr. Cacao butter is remarkable for the length of time it may be kept without becoming rancid.

In order to subject the acids which cacao butter contains to examination, it was saponified by caustic potash and the soap decomposed by muriatic acid. The melting point of the mixed acid was 125° Fahr.; they were then dissolved in hot spirits of wine and allowed to crystallize, when the crystals were collected and carefully dried by pressure. These solutions and crystallizations were repeated nine or ten times to free them from the less crystallizable acids, which remained dissolved in the alcoholic mother liquors. The crystals had then a melting point of 157° Fahr., and on analysis they proved to be stearic acid. The following are the results.

I.	0.318	gave	0.8835	carbonic acid,	and	0.3622	water.
II.	0.2595	„	0.719	„	„	0.300	„
III.	0.299	„	0.832	„	„	0.347	„

or per cent.

	I.	II.	III.
Carbon	76.82	76.61	76.85
Hydrogen ...	12.65	12.84	12.86
Oxygen	10.52	10.55	10.29
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

This gives the following formula for the hydrous acid :

		Per cent.
68	atoms of Carbon	5197.6
132	„ Hydrogen...	848.6
7	„ Oxygen	700.0
		<hr/>
		6746.2
		<hr/>
		100.00

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In order to determine the atomic weight of the acid the æther was prepared in the usual way, by dissolving a portion of stearic acid in alcohol and saturating it with muriatic acid gas.

The æther is a semi-transparent crystalline body, very like stearin. It was repeatedly washed with hot water to free it from muriatic acid. It was then carefully dried and subjected to analysis; the following are the results.

- I. 0·2715 gave 0·7595 carbonic acid, and 0·3155 water.
 II. 0·240 „ 0·671 „ „ 0·2805 „
 or per cent.

	I.	II.
Carbon	77·35	77·30
Hydrogen.....	12·91	12·94
Oxygen.....	9·79	9·76
	<hr/>	<hr/>
	100·00	100·00

The formula deducible from these analyses, $C_{72} H_{144} O_7$ is equivalent to 1 atom acid, 1 atom æther, and 1 atom water.

		Per cent.
72 atoms of Carbon ...	5503·3	77·49
144 „ Hydrogen	898·5	12·62
7 „ Oxygen...	700·0	9·86
	<hr/>	<hr/>
	7101·8	100·00

When one atom of æther and one of water are subtracted from the above,

we obtain the numbers

as the formula of anhydrous stearic acid :

		Per cent.
68 atoms of Carbon	5197·7	79·70
132 „ Hydrogen.....	823·6	12·58
5 „ Oxygen	500·0	10·38
	<hr/>	<hr/>
		100·00

When cacao butter is distilled it yields no appreciable quantity of sebacic acid, but when the uncrystallizable acid which remains in the alcohol out of which the stearic acid has crystallized is subjected to distillation, traces of sebacic acid are readily obtained. This indicates that the quantity of oleic acid contained in cacao butter is by no means very considerable.

I have every reason to believe that besides the stearic and oleic acids, cacao butter contains a third acid, which has a melting point of about 140° Fahr., and which may probably be the margaric. ? Its nature, however, must be the subject of some future investigation.