XII.—*On the Solid Fatty Acids of Coco-Nut Oil.* By G. CARR ROBINSON, F.R.S.E., *Demonstrator of Chemistry, Public Health Laboratory, University of Edinburgh.* (Plate XX.)

(Read 21st January 1878.)

Most common oils and fats are mixtures of ethereal salts, termed glycerides or glyceric ethers, formed from glycerine and acids of the fatty, the oleic, and other allied series.

Of the methods employed for the decomposition of oils and fats, the following are the most usual:—

1. Distillation of the oil or fat; those which yield *volatile* acids, such as the acetins, butyrins, &c., may be more or less distilled without decomposition; but those which yield *fixed* acids, *e.g.*, palmitin, olein, &c., are almost wholly decomposed by a heat of 300° C., yielding acrolein, numerous hydrocarbons, &c.

2. Distillation with dilute sulphuric acid, by which the volatile acids are separated from the non-volatile.

3. Distillation in a current of superheated steam, when the glycerides are decomposed, the fatty acids being liberated.

4. Saponification; oils and fats are decomposed by caustic alkalies into glycerine and a soap, the soap, when boiled with dilute sulphuric or hydrochloric acid, being decomposed into a sulphate or chloride of the alkali employed and the fatty acid set free.

To separate a mixture of fatty acids various methods are employed, of these may be mentioned—the separation of the *volatile* from the *fixed* acids by distillation; fractional distillation of the volatile acids; Liebig's method of partial saturation; whilst the *fixed* acids are separated by dissolving in alcohol and fractional precipitation with acetate of lead. Another method is that usually adopted in the preparation of ethereal salts, and consists in saturating with gaseous hydrochloric acid the alcoholic solution of the mixed acids, separating the ethers so produced by fractional distillation, saponifying the pure ethers, decomposing the soap, and examining the fatty acid by analysis, melting point, &c., or by converting it into baryta, silver, or lead salt, and examining these.

It was determined, at the suggestion of Dr LETTS and Dr CRUM BROWN, that an examination should be made in this manner of coco-nut oil.

Coco-nut oil or coco butter is obtained by pressure from the fruit of certain coco-palms. It is whitish, of unctuous consistence, with a peculiar fatty smell. It is a mixture of several glycerides, containing also free acids.

Though the frequent subject of investigation, this research into coco-nut

oil was undertaken with the view of ascertaining if the process of converting the mixed acids into ethers, and separating these by fractional distillation, would give results agreeing with those of other observers.

One of the most exhaustive memoirs on the constitution of coco butter is that by OUDEMANS (*Journal für Praktische Chemie*, lxxxi.). He saponified the coco butter with caustic potash, and from the potash soap obtained a lime salt by precipitating with ammonia and chloride of calcium; after treating the lime salt with ether, to remove any unsaponified fat, it is decomposed by hydrochloric acid, and the fatty acid, dissolved in alcohol, is subjected to fractional precipitation with acetate of baryta. In this way OUDEMANS obtained nine baryta salts; these were in turn decomposed by hydrochloric acid for the liberation of the fatty acids, the melting points of which were taken, and their composition arrived at by analysis. By this method OUDEMANS found in coco butter capric, caproic, caprylic, lauric, palmitic, and margaric acids, and denied the existence of cocinic acid ($C_{13}H_{26}O_2$).

Of other investigations of coco-nut oil may be mentioned those of BROMEIS (*Ann. Chem. Pharm.* xxxv.) and ST EVRÈ (*Ann. Chem. Phys.* xx.).

BROMEIS separated the acids by repeated crystallisation from alcohol; ST EVRÈ, in addition to this, prepared lead salts, extracted these with ether, and from them separated a body which was subjected afresh to crystallisation.

FEHLING (*Ann. Chem. Pharm.* liii.) obtained the volatile acids by distilling the coco butter with dilute sulphuric acid, saturating the distillate with baryta, and separating the baryta salts by their different solubility in water.

The following is the process employed in this research:—A quantity of coco butter, 5 kilograms, is melted with hot water, and boiled with a very weak soda lye for a period of eight hours; on cooling, the hard white soap is broken up, steam passed into it, and the soap solution boiled for another period of eight hours. After cooling the soap is well washed with cold water, then melted, hot water added, and the soap decomposed by the gradual addition of sulphuric acid. The fatty acids are separated from the sulphate of soda, glycerine, and excess of sulphuric acid, washed several times with boiling water, and again saponified, using at first a very weak lye. On cooling, the cake of hard soap is washed and decomposed with sulphuric acid as before.

The fatty acids so obtained, weighing about $3\frac{1}{2}$ kilograms, are thoroughly washed with hot water, dried, and dissolved in 1.25 kilograms of absolute alcohol, and the alcoholic solution saturated with gaseous hydrochloric acid; the ethers, separated from the water, dissolved again in alcohol, and a second time saturated with gaseous hydrochloric acid, washed from all trace of hydrochloric acid, dried first with chloride of calcium, and finally with phosphoric anhydride.

The mixture of ethers, dried in this manner, was then submitted to

fractional distillation ; the first distillation showed no trace of acrolein, whilst some previous experiments on the fractional distillation of fatty acids had to be abandoned owing to the continual production of this substance. Water, however, clung to the ether fractions with great obstinacy, and was with difficulty removed even by frequent treatment of the ethers with phosphoric anhydride.

This frequent treatment with phosphoric anhydride, along with the necessary drying of the distilling apparatus between each fractionation, entailed very considerable loss in ethers, so that the subjoined table of ether fractions, giving the weights of the various fractions after the ethers had been separated as much as was possible by distillation, must be accepted as representing only approximately the acids in coco-nut oil.

The quantities and boiling points of the seventeen ether fractions so obtained are represented on the diagram, the area of each blue rectangle representing the mass of the distillate between the temperature corresponding to the two ordinates. (Plate XX.)

Ether Fractions.

B Ether boiling point between 160° and 170° C. = 6 grammes.

C	„	„	170	180	10	„
E	„	„	180	190	9	„
	„	„	190	200	5	„
D	„	„	200	205	21	„
A	„	„	205	210	133	„
F	„	„	210	220	11	„
	„	„	220	230	8	„
H	„	„	230	240	15	„
I	„	„	240	250	8	„
J	„	„	250	260	16	„
	„	„	260	270	10	„
L	„	„	270	275	30	„
M	„	„	275	280	42	„
N	„	„	280	285	34	„
O	„	„	285	290	44	„
P	„	„	290	300	17	„

The ether marked B, boiling between 160° and 170° C., was now saponified by boiling with caustic soda, the solution of soap decomposed by sulphuric acid, the fatty acid separated, and washed to free it from sulphate of soda and excess of sulphuric acid used, then boiled with water and carbonate of baryta, filtered, the baryta salt crystallised out and purified by fractional crystallisation.

The baryta salts from ethers, ranging from B to L, were all obtained in this way ; the remaining four, M to P, were prepared by saponifying the ether, and after separating the fatty acid as before, dissolving this in alcohol, and boiling

it with an alcoholic solution of acetate of baryta, and, when possible, crystallising the new baryta salt from alcohol.

The following are the analyses of these baryta salts :—

The barium was estimated in the usual way, by igniting the salt with sulphuric acid, and weighing as BaSO_4 .

Analysis of baryta salt, marked A, from ether boiling between 205° and 210° C.

Five estimations of barium gave a mean of 32·50 per cent. barium.

Estimation of carbon and hydrogen ; combustion made with chromate of lead.

0·21625 grammes baryta salt gave—

0·337 grammes CO_2 = 42·54 per cent. carbon.

0·13075 „ H_2O = 6·70 „ hydrogen.

Allowing for the carbon retained by the baryta as BaCO_3 , and adding this to the carbon found, gives 45·31 per cent. carbon in salt,* thus—

100 grammes baryta salt yields, on analysis, 32·5 grammes Ba.

0·21625 grammes of salt (quantity used in combustion) = 0·07028 grammes Ba. And

137 grammes Ba require 44 grammes CO_2 to form BaCO_3 .

∴ 0·07028 grammes Ba require 0·0225 grammes CO_2 .

0·0225 + 0·337 (CO_2 found) = 0·3595 grammes CO_2 .
= 45·31 per cent. carbon.

Analysis of baryta salt, marked A—

Carbon,	45·31
Hydrogen,	6·70
Barium,	32·50
Oxygen (by difference),	15·49
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	100·00

Agreeing with barium caprylate $(\text{C}_8\text{H}_{15}\text{O}_2)_2\text{Ba}$, which requires—

Carbon,	45·39
Hydrogen,	7·09
Barium,	32·38
Oxygen,	15·14
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	100·00

A weighed quantity of this salt, A, on being exposed for three hours to 100° C., did not lose weight ; it is therefore anhydrous.

* Explanation of this will be found at end of analyses of these salts.

From the acid obtained from ether, marked H, boiling point 230° to 240° , both a baryta and a lead salt were prepared.

Baryta salt, marked H, gave 28.53 per cent. Ba.

Analysis of lead salt, marked H.

0.3805 grammes lead salt gave—

0.60625 grammes CO_2 = 43.45 per cent. carbon.

0.252 „ H_2O = 7.35 „ hydrogen.

0.20225 grammes lead salt gave, after ignition with sulphuric acid,—

0.10775 grammes PbSO_4 = 38.03 per cent. lead.

Analysis of lead salt, marked H—

Carbon,	43.45
Hydrogen,	7.35
Lead,	38.03
Oxygen (by difference),	11.17
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	100.00

Agreeing with lead caprate $(\text{C}_{10}\text{H}_{19}\text{O}_2)_2\text{Pb}$, which requires—

Carbon,	43.71
Hydrogen,	6.90
Lead,	37.70
Oxygen,	11.69
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	100.00

Barium caprate $(\text{C}_{10}\text{H}_{19}\text{O}_2)_2\text{Ba}$ requires—

28.60 per cent. barium.

Analysis of baryta salt, marked N, from ether boiling point, 280° to 285° C.

This salt is anhydrous. 0.233 grammes salt, exposed for two hours to 100° C., did not lose in weight.

Three estimations of barium gave a mean of 25.40 per cent. Ba.

Estimation of carbon and hydrogen; combustion made with oxide of copper.

I. 0.05025 grammes baryta salt gave—

0.093 grammes CO_2 = 51.36 per cent. carbon.

0.04325 „ H_2O = 9.56 „ hydrogen.

II. 0.323 grammes baryta salt gave—

0.6045 grammes CO_2 = 51.04 per cent. carbon.

0.25125 „ H_2O = 8.66 „ hydrogen.

III. 0.1905 grammes baryta salt gave—

0.35775 grammes CO_2 = 51.21 per cent. carbon.
 0.1545 „ H_2O = 9.00 „ hydrogen.

Allowing for carbon retained, as BaCO_3 (as in A), these show respectively—

I. Carbon,	.	.	.	.	.	53.28
II. „	.	.	.	.	.	53.67
III. „	.	.	.	.	.	53.45

	I.	II.	III.
Carbon, . . .	53.28	53.67	53.45
Hydrogen, . .	9.56	8.66	9.00
Barium, . . .	25.35	25.57	25.34

Agreeing with barium laurate $(\text{C}_{12}\text{H}_{23}\text{O}_2)_2\text{Ba}$, which requires—

Carbon,	53.82
Hydrogen,	8.59
Barium,	25.60
Oxygen,	11.99
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	100.00

Analysis of baryta salt, marked O, from ether, boiling point 285° to 290° C.
 Two estimations of barium gave—

25.09 and 25.26 per cent. barium.

Estimation of carbon and hydrogen; combustion made with chromate of lead.

I. 0.13175 grammes baryta salt gave—

0.25625 grammes CO_2 = 53.39 per cent. carbon.
 0.10975 „ H_2O = 9.25 „ hydrogen.

II. 0.17675 grammes baryta salt gave—

0.34525 grammes CO_2 = 53.27 per cent. carbon.
 0.141 „ H_2O = 8.86 „ hydrogen.

Allowing for carbon retained as BaCO_3 (as in A and N), these show—

I. 55.11, and II. 55.46 per cent. carbon.

	I.	II.
Carbon,	55.11	55.46
Hydrogen, . . .	9.25	8.86
Barium,	25.09	25.26

Agreeing with barium cocinate ($C_{13}H_{25}O_2$)₂Ba, which requires—

Carbon,	55.41
Hydrogen,	8.88
Barium,	24.33

The last analyses to be mentioned are those of baryta salt, marked P, from ether, boiling point 290° to 300°.

Analysis shows this salt to be the same as O.

Two estimations of barium gave—

25.10 and 24.63 per cent. barium.

Estimation of carbon and hydrogen ; combustion made with chromate of lead.

I. 0.2095 grammes baryta salt gave—

0.407 grammes CO₂ = 52.98 per cent. carbon.
0.1685 „ H₂O = 8.93 „ hydrogen.

II. 0.1405 grammes baryta salt gave—

0.2725 grammes CO₂ = 52.89 per cent. carbon.
0.1175 „ H₂O = 9.28 „ hydrogen.

III. 0.551 grammes baryta salt gave—

1.0765 grammes CO₂ = 53.26 per cent. carbon.
0.412 „ H₂O = 8.29 „ hydrogen.

Allowing for carbon retained as BaCO₃ (as in A, N, and O), these show—

	I.	II.	III.
Carbon, . . .	55.10	55.06	55.40

Analysis—

	I.	II.	III.
Carbon, . . .	55.10	55.06	55.40
Hydrogen, . . .	8.93	9.28	8.29
Barium, . . .	25.10	24.63	

To prove that the corrections made in the carbon determinations of these analyses were not only justifiable but necessary, two analyses were made of the same baryta salt P with chromate of lead mixed with one-tenth of its weight of fused bichromate of potash, with the following results :—

I. Carbon,	55.40 per cent.
II. Carbon,	55.39 „

These agree well with carbon percentage demanded by formula $(C_{13}H_{25}O_2)_2 Ba$. Theory, 55·41 ; found 55·40 and 55·39.

These results show conclusively that when the combustion of baryta salts of the higher fatty acids is made with chromate of lead, that not only is the "carbon found" *always* less than that demanded by theory, but also that the deficiency in carbon is exactly accounted for by *all* the barium being left as carbonate, hence it is absolutely necessary to employ, along with chromate of lead, some other substance that readily gives up oxygen, such as bichromate of potash.

A mixture of fused borax and oxide of copper has been recommended in the analyses of salts such as these. Experiments made with this mixture were very unsatisfactory, the "carbon found" being the same as when oxide of copper alone is used.

The analysis of these baryta salts, prepared from the ethers, shows the presence of the same fatty acids as those found by other observers and by other methods.

OUDEMANS denies the presence of the acid $C_{13}H_{26}O_2$, cocinic acid, in coco butter, and doubts the existence of such an acid ; whilst BROMEIS and ST EVRÈ both found an acid, melting point $35^\circ C.$, and having the formula $C_{13}H_{26}O_2$.

FEHLING found in coco-nut oil an acid resembling, in appearance and melting point, that prepared by BROMEIS.

HEINTZ considers this acid a mixture on account of its low melting point, which is lower than that of lauric acid, $C_{12}H_{24}O_2$, whereas it should be intermediate between that of lauric acid, melting point $44^\circ C.$, and myristic acid, melting point $54^\circ C.$; he finds, moreover, that a mixture of these two acids in the proportion of fourteen parts of lauric to two parts of myristic does melt at about $35^\circ C.$

On the other hand, the existence of this acid, $C_{13}H_{26}O_2$, in coco butter is confirmed by the analysis of the baryta salt marked P ; the formula $(C_{13}H_{25}O_2)_2 Ba$, as already shown, requiring

Carbon,	.	.	.	.	.	.	.	55·41
Hydrogen,	.	.	.	.	.	.	.	8·88
Barium,	.	.	.	.	.	.	.	24·33

whilst these analyses, made with a mixture of chromate of lead and bichromate of potash, show—

		I.	II.
Carbon,	.	55·40	55·39

also the acid, from which this baryta salt was prepared, had a melting point of $45^\circ C.$, and solidifies at very nearly the same temperature.

Having thus shown in this research the existence in coco butter of acids proved by others to be present, the process of converting the mixture of fatty acids into ethers, and separating these by fractional distillation, may be considered generally applicable for the examination of ordinary oils and fats.

In this investigation the chief difficulties met with were, first, in saponifying the coco-nut oil, when it was found that only by prolonged boiling with a weak lye, decomposing the soap, and boiling for a second time with caustic soda, was complete saponification effected; secondly, there was great difficulty experienced in thoroughly drying the ethers, even phosphoric anhydride, as already mentioned, only removing the water after prolonged contact with them. Chloride of calcium was of no use for drying them, and baryta could not be employed, as at ordinary temperature it slowly decomposes the ethers.

As before remarked, the accompanying diagram (Plate XX.) shows the ether-fractions after distillation had been carried on, until no longer any appreciable separation was effected. The rectangular areas represent the quantity in grms. of distillate between given intervals of temperature, whilst the curve represents what may be supposed to be the limit when the intervals of temperature are indefinitely diminished.

Such a curve is obviously of a highly characteristic appearance, depending upon the nature of the simple fats and the proportion in which they occur in the original mixture; and it is possible that curves such as this may be of use in identifying particular mixtures of volatile substances.