

III.—*The Chemistry of Cocoa Butter. Part I. Two New Fatty Acids.*

By CHARLES T. KINGZETT.

SOME few months ago I commenced, at the suggestion of my friend, Dr. B. H. Paul, an investigation upon the chemistry of cocoa butter, and although my work has had many interruptions, some interesting and important results have been attained; so important indeed have been these results, that I am induced to publish this paper, which otherwise must be regarded as of a preliminary nature.

The sample of cocoa butter upon which I worked was obtained from Messrs. Cadbury and Sons. It was a hard, imperfectly transparent, slightly yellowish solid, melting at about 30°C. , and when once melted, retaining the liquid state for some time at a temperature below that just mentioned. To alcohol of 85 per cent. and maintained at the boiling point, it gave up but traces of soluble matter, and from the fact that hot ammonia water extracted from it but traces of matter, I conclude that it is practically or entirely free from fatty acids, as such.

It was proved by special experiments to be also entirely free from volatile or soluble fatty acids.

1st Experiment.—40 grams were saponified by caustic soda solution, the mixture nearly neutralised with dilute sulphuric acid, and the precipitate of sodium salt washed after filtration. It was dissolved in much boiling water, and was then precipitated by barium chloride solution.

An attempt was made to estimate the oleate of barium contained in this salt, by extraction with boiling alcohol; but that employed (of 85 per cent.) dissolved some considerable quantity of a barium salt other than the oleate, whose free acid was solid at ordinary temperatures. I also attempted to estimate the oleic acid by converting the barium salt into lead salt, and extracting this by ether, but in course of the extraction the salt became yellow, and something more than mere oleate of lead dissolved.

The lead precipitate insoluble in ether was reconverted into barium salt, through the intervention of an ammonium soap made from the free acids and the barium salt analysed—

(1.) 0.495 grm. dry at 100° C. gave 1.048 grm. CO₂, and 0.427 grm. H₂O.

(2.) 0.4190 grm. gave 0.1490 BaSO₄.

Synopsis of Analysis :—

C	57.74
H	9.58
Ba	20.90
O	11.78

If we deduct the barium we get by calculation the following percentages for the free acid :—

C	73.00
H	12.11
O	14.89

The barium salt was now decomposed by hydrochloric acid in presence of ether, and the free acids obtained by distillation of the ether were recrystallised from alcohol. The first crop was lost; the second, which was evidently impure (being slightly coloured), was analysed; 0.212 grm. gave 0.545 grm. CO₂ and 0.237 grm. H₂O.

C	70.11
H	12.42
O	17.47

2nd Experiment.—Another quantity of cocoa butter was now saponified and the sodium salt made into barium salt. This was decomposed by hydrochloric acid in presence of ether, and the fatty acids obtained by distillation of the ethereal solution crystallised from 85 per cent. alcohol containing animal charcoal in suspension; the last mother-liquor was retained.

The solid acid obtained, as described, was a snow-white powdery substance when dry.

It was recrystallised from alcohol, two successive crops being obtained; the first by deposition; the second after concentration.

The first crop had a melting point of 65° .

(a.) 0.164 grm. dried at 100° C., and burnt with PbCrO_4 , with the aid of KClO_3 , gave 0.197 grm. H_2O and 0.464 grm. CO_2 .

(b.) 0.125 grm. gave 0.147 grm. H_2O and 0.353 grm. CO_2 .

Synopsis :—

	a.	b.
C.....	77.16	77.01
H	13.35	13.06
O	9.49	9.93

This same mixture of acids (for such it eventually proved to be) was afterwards fractionated by recrystallisation from spirit into three portions, 1, 2, and 3, which were analysed.

Fraction 1. Melted at 68° .

(a.) 0.185 grm. gave 0.223 grm. H_2O , and 0.521 grm. CO_2 .

(b.) 0.159 grm. gave 0.188 grm. H_2O .

C.....	76.81
H.....	13.35 and 13.14.
O.....	9.84

Fraction 2. Melted at 61° .

0.138 grm. gave 0.3960 CO_2 and 0.162 H_2O .

C.....	78.26
H.....	13.04
O.....	8.70

Fraction 3. Melted at 58° .

0.157 grm. gave 0.410 grm. CO_2 , and 0.182 H_2O .

C.....	71.22
H.....	12.87
O.....	15.91

The second crop (following that which furnished these three fractions) was fractionated into two portions, each melting at 58° .

The oleic acid contained in cocoa butter was isolated from the last mother-liquor alluded to above, and obtained after these successive crops of solid fatty acids. It was made into ammonium salt, and this into barium salt, which was dried and extracted by alcohol. The powder thus obtained on cooling of the alcoholic extract was snow-white.

0.322 gave 0.105 $\text{BaSO}_4 = 19.25$ per cent. Ba.

Inasmuch as oleate of barium gives 19.59 per cent. Ba, and further seeing this acid had also the other properties of ordinary oleic acid, there is no reasonable doubt left regarding its true nature.

3rd Experiment.—Another quantity of cocoa butter was now saponified; the sodium soap washed slightly, and decomposed by sul-

phuric acid; the free acids were washed by repeated meltings with hot water, then dried and weighed. Weight = 37 grms.

It was recrystallised from alcohol in the presence of charcoal, and the mother-liquors treated as described below.

Four successive crops of fatty acids were obtained: (*a*) shortly after cooling to some extent; (*b*) on standing; (*c*) by concentration of mother-liquor; (*d*) after last fraction on standing. The first crop was further fractionated by alcohol into three portions, and the third crop into two portions; the mother-liquors being for the time disregarded.

Examination of the three fractions from first crop:—

(1.) Melted at 70.5° .

(2.) Melted at 70.8° .

(3.) Melted at 61.0° .

The first portion melting at 70.5° C. was again fractionated with two crops.

(*a.*) Melting at $71-71.5^{\circ}$ C., and (*b*) melting at $71-71.5^{\circ}$ C.

Analysis of (a):—

0.179 grm. gave 0.518 CO_2 , and 0.219 H_2O .

C 78.92

H 13.59

O 7.49

This product was eventually further fractionated into two portions, the first of which was analysed.

It melted at 72.2° , solidified again at 69° .

(*a.*) 0.170 grm. gave 0.515 CO_2 and 0.213 H_2O .

(*b.*) 0.069 „ 0.208 „ „ 0.088 „

(*a.*) C. 82.62 (b.) 82.21.

H. 13.92 14.16.

O. 3.46 3.63.

The second crop melted at 66° C.

The third crop melted at 56.5° C.

This last crop was further fractionated into two portions and a mother-liquor.

Portion (*a*) melted at 59 to 59.5° C., and (*b*) at 57.5 to 58° C.

Analysis of (b):—

0.204 grm. gave 0.542 CO_2 and 0.257 H_2O .

C 72.46

H 13.99

O 13.55

To recapitulate, we may here show in tabular form the percentage composition and melting points of the foregoing products:—

1.	2.	3.	4.	5.	6.	7.	8.	9.
M. p... 57—58°	58·5°	57·5°	—	68°	65°	61°	71·5°	72·2
C 70·11	71·22	72·46	73·00	76·81	77·16	78·26	78·92	82·62
H 12·42	12·87	13·99	12·11	13·14	13·06	13·04	13·59	13·92
O 17·47	15·91	13·55	14·89	10·05	9·88	8·70	7·49	3·46

Neglecting the intermediate terms, and taking the extremes reacted by the method employed, these latter are tolerably well represented by the formulæ, $C_{12}H_{24}O_2$ and $C_{64}H_{128}O_2$:—

	$C_{12}H_{24}O_2$.	$C_{64}H_{128}O_2$.
C	72·00	82·75
H	12·00	13·79
O	16·00	3·46
	<hr/> 100·00	<hr/> 100·00

Now of the products whose analyses are described above, only one was at all coloured, and that was the one containing 70·11 per cent. ; moreover, this was the only one which was burnt with $PbCrO_4$ without the supplemental aid of potassic perchlorate, therefore, neglecting this, the nearest analyses approaching those just given are—

	$C_{12}H_{24}O_2$.		$C_{64}H_{128}O_2$.
C	71·22		82·62
H	12·87	and	13·92
O	15·91		3·46
	<hr/> 100·00		<hr/> 100·00

$C_{12}H_{24}O_2$ is the formula of lauric acid, which, however, has a melting point of 43°. As the lowest melting point I have yet observed among the fatty acids from cocoa butter is 57·5°, the fatty acid to which it belongs, if lauric acid, must contain some quantity of an acid of higher melting point than lauric acid. Therefore, the acid itself would be lower in the series $C_nH_{2n}O_2$ than lauric acid.

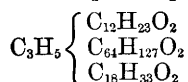
Further, the highest acid previously known in the series $C_nH_{2n}O_2$, is melissic acid, $C_{30}H_{60}O_2$, and whereas I have described a definitely crystalline substance of the empiric formula $C_{64}H_{128}O_2$, it is by far the highest acid term in the series, yet discovered.

But I would not claim to have attained as yet the ultimate limits in either direction ; the higher acid may contain more than 64 atoms of carbon to the molecule, and the lower one may contain less than 12 atoms to the molecule. I have, however, exhausted the capabilities of the only process yet used by me ; in the future, I intend to apply whatever other methods are available among those known, or in my power to devise.

It only remains for me to add that I have prepared barium, calcium, and silver salts of the higher acid, but refrain from publishing their percentage composition until more ultimate possibilities may have been attained. I may mention, however, that the silver salt is coloured only slightly by light, and is deposited by precipitation from an ammoniacal solution by argentic nitrate as a gelatinous mass, which, when dry, is highly electric and quite insoluble in alcohol of 85 per cent. and in ether. The higher fatty acid itself also appears to be somewhat electric; it crystallises in granules from a concentrated alcoholic solution, but in microscopic needles from a more dilute solution. At high temperatures it distils apparently unchanged. The crystalline character of the lower acid is more distinct, and sometimes it is obtained in beautiful pearly plates, and at others in fine long needles.

In the third experiment I determined, approximately, the amount of oleic acid contained in the 37 grams of total fatty acids from cocoa butter, by separating, as far as could be, all crystallisable solid fatty acids from the ultimate mother-liquors after recrystallisation. It amounted to about 20 per cent. of the total.

So far as I have ascertained, and merely for the sake of a calculation, it may be stated that a compound glyceride of the composition



requires exactly 20 per cent. oleic acid to be furnished by the total acids derivable from it.

At the same time, it may be that cocoa butter is a mixture of the three glycerides, or even of more, whose fatty acids in such case form part of the intermediate crops not yet analysed.

Before concluding the paper, it should be stated that I have in vain searched chemical literature with the view of discovering any publication bearing upon my subject. But the only matter I have been able to find is a statement made in nearly all works to the effect that cocoa butter yields almost exclusively stearic acid, and the evidence of its purity when prepared is a permanent melting point of 69 to 70° C. It appears, therefore, that the melting point has hitherto been accepted as sufficient evidence of the presence of stearic acid; but, as will be seen from my investigation, this is entirely incorrect. Compared with the formula of the highest product I have obtained from cocoa butter, the melting point of 72·2° appears to be low, but it is impossible that the acid can contain less than 64 atoms of carbon, and should its melting point be regarded in any way as a difficulty, the acid could, of necessity only, be still higher in the series than so far ascertained. Without waiting until its molecular weight shall have been definitely

established, I propose for it the name of *Theobromic acid*, which recalls the source from which it is obtained, namely, the fat of the seeds of *Theobroma Cacao*. The seeds are known to yield from 30 to 50 per cent. of this fat.
