The constituents of chaulmoogra seeds / by Frederick B. Power and Frank H. Gornall.

Power, Frederick B. 1853-1927.
Gornall, Frank H.
Wellcome Chemical Research Laboratories.

London : Wellcome Chemical Research Laboratories, [1904] No. 45.

THE CONSTITUENTS
OF
CHAULMOOGRA SEEDS

BY

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AND

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(From the Transactions of the Chemical Society, 1904)

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LXXXV.—*The Constituents of Chaulmoogra Seeds.*

By Frederick Belding Power and Frank Howorth Gornall.

It has, until quite recently, been assumed that the seeds yielding the so-called "chaulmoogra oil"—a fatty oil, which is largely used in the treatment of leprosy and various skin diseases—are derived from *Gynocardia odorata* (R.Br.), a tree belonging to the family of *Bixaceæ*, and indigenous to the Malayan Peninsula and North-Eastern India (compare "Pharmacographia Indica," Vol. I, p. 142). It is now known, however, that this oil is obtained from the seeds of *Taraktogenos*

Kurzii (King), a plant which is a native of Burmah (*Pharm. J.*, 1900, **64**, 522, and 1901, **66**, 596).

The investigation of chaulmoogra seeds appears hitherto to have been restricted to the fatty oil, obtained from them by expression, and the first chemical examination of the latter is embodied in a paper by Moss (*Year-book of Pharmacy*, 1879, pp. 523—533). The oil examined by Moss was apparently a commercial product, as he gives no indication of having prepared it himself. He states that it had a melting point of 42° and a specific gravity at that temperature of 0·930. On hydrolysis, it afforded him 81·1 per cent. of fatty acids, which were considered to consist approximately of "gynocardic acid," 11·7; palmitic acid, 63·0; hypogæic acid, 4·0; and "cocinic" (undecylic) acid, 2·3 per cent., contained in the oil as glyceryl esters, the first two being also present in the free state. The melting point of the mixed acids was 44°. The methods adopted for the separation and identification of the above-mentioned acids were not such, however, as to render the results at all conclusive. The so-called "gynocardic acid" is of interest, for the reason that a preparation bearing this name has been an article of commerce for some years, and is employed medicinally. It was stated by Moss to separate from weak alcohol in crystalline plates melting at 29·5°. From the results of two analyses, the formula $C_{14}H_{24}O_2$ was deduced, although it was clearly indicated that additional data would be required in order to determine the correctness of this supposition.

Petit (*J. Pharm. Chim.*, 1892, **26**, 445) has published a method for the preparation of "gynocardic acid," and under this name he appears to comprehend that portion of the total fatty acids which is soluble in 70 per cent. alcohol at about 15°, and has a melting point of 29°, which is practically that assigned to it by Moss.

Schindelmeiser (*Ber. deutsch. pharm. Ges.*, 1904, **14**, 164) has published a short paper entitled "Gynocardia Oil," in which he appears to have accepted in general the conclusions of Moss respecting its constituents, but without any confirmatory evidence of their correctness, although he gives the melting point of the "cold-expressed" oil as 26°. He also retains the name of gynocardic acid for a substance which was prepared according to Petit's method (*loc. cit.*), and, after purification with ether, melted at 29·5°. It was considered probable that the substance thus separated had the formula $C_{21}H_{40}O_2$, although this supposition appears to have been based only on a titration and the analysis of a silver salt, and it was shown to be unsaturated. He furthermore assumes, with some reservation, that, besides palmitic, hypogæic, and "cocinic" acids, the crude acids contain a hydroxy-acid, the evidence for the presence of the latter being deduced from a determination of the acetyl value (207·8) and from the high iodine value (110·8).

EXPERIMENTAL.

An opportunity having been afforded us of obtaining a large quantity of fresh Chaulmoogra seeds, which had been brought into the London market, it was decided to make a complete investigation of them. They were identified as the product of *Taraktogenos Kurzii* (King).

On bruising the seeds, it was observed that a strong odour of hydrocyanic acid was developed. This indicated that it existed in the form of some unstable compound which became hydrolysed through the action of an enzyme. The hydrocyanic acid, after being further identified by qualitative tests, was quantitatively determined as follows: a quantity of the bruised kernels was digested with water for two days in a tightly-closed flask at a temperature of about 23°; steam was then passed through the liquid and the distillate titrated with a decinormal solution of silver nitrate. The amount of hydrocyanic acid corresponded with 0·036 per cent. of the weight of the kernels. When the seeds have been kept for some time, even in a dry place and with the shells unbroken, they no longer furnish hydrocyanic acid in contact with water or by the action of dilute acids.

In operating with several hundredweights of the seeds, the shells, which were first separated, represented 34 per cent. of their weight. The kernels, when subjected to powerful hydraulic pressure, yielded an amount of fixed oil corresponding with 30·9 per cent. of the entire seed. The residual "press-cake" represented 32·2 per cent. of the original weight of the seeds. A portion of the kernels, when completely extracted with ether in a Soxhlet apparatus, afforded 55 per cent. of their weight of fixed oil, corresponding with 38·1 per cent. of the entire seed (having 30·7 per cent. of shells).

Examination of the "Press-cake."

This material, when received directly from the press, exhaled a large amount of hydrocyanic acid, and, when kept for a comparatively short time, the compound from which the latter substance was developed became completely decomposed.

Isolation of a Hydrolytic Enzyme.

A portion of the press-cake was digested with water at the ordinary temperature and expressed. To the clear, filtered liquid about twice its volume of alcohol was added, when an abundant, light-coloured, flocculent precipitate was obtained, which was collected, washed with a little alcohol, and dried in a desiccator over sulphuric acid When dry, it formed a dark brown mass, which could be reduced to a light brown powder. This substance gave the usual reactions characteristic of proteids. It hydrolysed amygdalin with the production of benzaldehyde and hydrocyanic acid, and with potassium myronate it yielded mustard oil. On heating its aqueous solution to boiling, its hydrolytic properties were destroyed. The enzyme has apparently only very little action in effecting the hydrolysis of the fat contained in the seed.

Search for a Glucoside.

A quantity of the press-cake was extracted with light petroleum, for the more complete removal of the fatty oil, and subsequently with hot alcohol. After the removal of the alcohol, the extract was mixed with water, purified by basic lead acetate, the excess of lead precipitated by hydrogen sulphide, and the liquid finally concentrated under diminished pressure. A light brown syrup was thus obtained, which developed hydrocyanic acid by contact with the enzyme or other hydrolytic agents, and reduced Fehling's solution on boiling. It afforded an osazone melting at 205°, which was evidently a phenylglucosazone.

The syrupy liquid showed no tendency to crystallise, even after a long time, and no crystalline substance could be extracted by treatment with various solvents. A portion of the liquid was boiled in a reflux apparatus with dilute sulphuric acid, and subsequently distilled. The distillate contained a large amount of hydrocyanic acid, but no aldehyde or ketone could be detected. The acid liquid remaining in the flask was extracted with chloroform, which yielded only a very slight syrupy residue. It was then digested with barium carbonate in order to remove the sulphuric acid, filtered, decolorised with animal charcoal, and concentrated under diminished pressure. A viscid liquid containing a large amount of sugar was thus obtained, but no crystalline substance.

Although it has not yet been found possible to isolate either this cyanogenetic compound or any hydrolytic product of an aldehydic or ketonic nature, some further experiments will be made in this direction.

Volatile Constituents of the Alcoholic Extract.

A large quantity of the press-cake, which no longer contained any hydrocyanic acid or the compound affording it, was extracted with hot alcohol. After distilling off the alcohol, a soft, dark brown extract was obtained, which had the characteristic odour of the seed and contained a considerable proportion of fatty oil.

Two kilograms of this extract were distilled in steam. The acid distillate, which contained a few oily globules, was extracted with ether, and on removing the latter a small amount of a highly aromatic, yellow, oily liquid was obtained, which evidently consisted of a mixture of volatile acids and esters, but distilled over too wide a range of temperature to permit of their further investigation. The acid remaining in the distillate was converted into a barium salt, and from this a silver salt was prepared, the chief portion of which was soluble in hot water and crystallised on cooling.

0·1008 gave 0·0652 Ag. Ag = 64·7.
$C_2H_3O_2Ag$ requires Ag = 64·7 per cent.

This volatile acid was therefore acetic acid.

The extract was then repeatedly treated with hot water, the mixture allowed to cool, and placed on a strainer. A considerable amount of solid fatty matter was thus separated from a dark aqueous liquid, in which some viscid oil was suspended. The solid fat yielded on hydrolysis a quantity of fatty acids, which are probably identical with those contained in the oil expressed from the seeds, and contain a very small amount of formic acid. The aqueous liquid strained from the solid fat was extracted with chloroform, which removed a large amount of oily substance; this was hydrolysed with alcoholic potassium hydroxide, the alcohol removed, the residual potassium salt taken up with water, and the strongly alkaline liquid extracted with ether. The combined ethereal liquids were washed with a little water, dried, and the ether removed. An oily liquid which was thus obtained was fractionally distilled under 18 mm. pressure, and thus resolved into (1) a very small fraction which passed over below 212°; (2) the principal fraction, which boiled between 212° and 220°; (3) a small fraction between 220° and 240°, but which passed over chiefly at 220—225°; and (4) a small amount of dark residue containing a little phytosterol (compare p. 844).

In order to ensure the complete freedom of this neutral liquid from any trace of fatty acids arising from the dissociation of their alkali salts in the process for its separation, the above-mentioned fraction, 212—220°/18 mm., was dissolved in ether and the solution shaken out many times with a concentrated solution of potassium hydroxide. The ethereal liquid was then washed, dried, the ether removed, and the residual, light yellow oil again distilled. It passed over almost entirely at 213—220°/18 mm., as a nearly colourless, odourless liquid, the greater portion distilling at 214—215°/18 mm. A portion boiling at the latter temperature was taken for analysis and the determination of its constants.

0·1403 gave 0·3967 CO_2 and 0·1455 H_2O. C = 77·1; H = 11·5.
0·1053 „ 0·2989 CO_2 „ 0·1100 H_2O. C = 77·4; H = 11·6.

0·1087 gave 0·3077 CO_2 and 0·1139 H_2O. C = 77·2; H = 11·6.
$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent.

Its density was 0·9066 at 16°/16°. In a 1 dcm. tube, it gave α_D + 38°27′, whence $[\alpha]_D$ + 42·4°.

This substance, on account of its method of isolation and purification, can be neither an acid nor a lactone. As it could be recovered unchanged after boiling with acetic anhydride and sodium acetate, it is also not an alcohol. It is unsaturated, and would appear to contain one ethylenic linking.

0·6460 required 0·5997 iodine. I = 92·8.
$C_{18}H_{32}O_2$, with one ethylenic linking, requires I = 90·7 per cent.

It has not yet been definitely determined to what class of compounds this substance belongs, but from some results which will be communicated later it may be stated that in all probability it is either an unsaturated, open chain diketone or a partly cyclic, unsaturated keto-ether. The occurrence in nature of substances conforming with either of these types has apparently not hitherto been observed.

The strongly alkaline solution of potassium salts from which the above-described neutral liquid had been extracted by ether was acidified with sulphuric acid, when some solid fatty acids separated. On distilling the liquid, a volatile acid was obtained which was converted into its barium salt, the reactions and analysis of the latter showing it to be formic acid.

The Fatty Oil (Chaulmoogra Oil).

At the ordinary temperature, this is a soft solid, having a faintly yellow colour and a characteristic odour. Its constants were determined with the following results.

	Expressed oil.	Oil extracted by ether.
Melting point	22—23°	22—23°
Specific gravity	0·951 at 25° 0·940 at 45°	0·952 at 25° 0·942 at 45°
$[\alpha]_D^{15°}$	+52·0°	+51·3°
Acid value	23·9	9·5
Saponification value ...	213·0	208·0
Iodine value..............	103·2	104·4

Hydrolysis of the Fatty Oil. Identification of Phytosterol and Glycerol, and Separation of the Fatty Acids

One hundred grams of the expressed oil were hydrolysed by boiling with an excess of alcoholic potash. After the removal of some of the alcohol, the dark liquid was mixed with sand and the mixture heated until quite dry, when it was brought into a Soxhlet apparatus and extracted with light petroleum. After the removal of the petroleum, a residue was obtained which consisted of a small amount of a crystalline substance associated with some light yellow, gummy matter having a cinnamon-like odour. By dissolving the product in warm ethyl alcohol and cooling the solution, the crystalline substance was separated from the amorphous matter, and, after several crystallisations from ethyl alcohol, was obtained in the form of white, glistening needles melting at 132°.

0·0694 gave 0·2128 CO_2 and 0·0760 H_2O. C = 83·6 ; H = 12·2.
0·1861 ,, 0·5704 CO_2 ,, 0·2007 H_2O. C = 83·6 ; H = 12·0.
$C_{26}H_{44}O$ requires C = 83·9 ; H = 11·8 per cent.

The substance thus has the formula and melting point of phytosterol, and its identity was further confirmed by the colour reactions characteristic of the cholesterol group.

For the identification of glycerol as a product of hydrolysis of the oil, the mixture in the Soxhlet apparatus was extracted several times with hot water. The cold, alkaline, aqueous liquid was then acidified with sulphuric acid, and the fatty acids, which separated as a nearly white, solid cake, were collected by filtration. The acid filtrate was then treated with barium carbonate, in order to remove the sulphuric acid, and evaporated. By subsequently mixing the residue with alcohol, again concentrating as far as possible and repeating this operation several times, a residue was obtained from which alcohol extracted 6 grams of glycerol, which, on distillation under 18 mm. pressure, passed over at 185°.

0·0898 gave 0·1270 CO_2 and 0·0710 H_2O. C = 38·6 ; H = 8·8.
$C_3H_8O_3$ requires C = 39·1 ; H = 8·7 per cent.

The Fatty Acids.

The foregoing solid fatty acids were dissolved in ether, the solution dried, and the ether removed ; the residue, which soon formed a solid cake, weighed 90 grams. For the determination of the constants of the mixture of fatty acids thus obtained, a quantity of the dried product was first heated in a steam oven and then exposed over paraffin wax in a vacuum desiccator in order to eliminate the last trace of ether. The solidified product then melted at 44—45°, had a specific rotatory power $[\alpha]_D$ $+52{\cdot}6°$ in chloroform, the "acid value" 215, and the "iodine value" 103·2.

The absence of hydroxy-acids in this mixture was proved by the fact that, on treatment with acetic anhydride according to Lewkowitsch's method (*J. Soc. Chem. Ind.*, 1890, **9**, 846), no acetylation took place.

Fractional Crystallisation of the Fatty Acids.

For the examination of the fatty acids, which obviously represented a mixture of substances, 7250 grams were dissolved in 20 litres of hot 94 per cent. alcohol. When left overnight, the cold solution yielded 2300 grams of a distinctly crystalline acid. This was again crystallised, in the first instance from alcohol (90 per cent.), and finally from light petroleum, when 1100 grams of an acid were obtained which separated from the latter solvent in glistening leaflets melting at 68°, and this melting point remained unaltered by further crystallisations from a variety of solvents.

By removing the solvent from the first of the last two mother liquors, 800 grams of residue remained. In order to eliminate a small amount of resinous matter, and thus obtain the substance in a form better adapted for analysis and the determination of constants, a portion was dissolved in an alcoholic solution of potassium hydroxide, the solution concentrated as far as possible, the potassium salt dissolved in water, and the solution extracted several times with light petroleum. The aqueous solution was then acidified, the liberated acids taken up with ether, the ethereal solution washed, dried, and the solvent removed, in the first instance by distillation, and subsequently by exposure of the warm, melted acid in a vacuum desiccator over paraffin wax. The white, solid acids thus obtained melted at 34—35°.

The last-mentioned, petroleum mother liquor was also treated in a similar manner. The residue, after the removal of the solvent, weighed 400 grams, and, after purification from resinous matter, the melting point of the fraction was 59—61°.

Having initially separated a large amount of an individual acid (m. p. 68°), which will subsequently be described, the first mother liquor was diluted with a small volume of water, which precipitated a quantity of substance, and this was again dissolved by raising the temperature a few degrees. On cooling, there separated from this solution a fraction of solid acids which weighed 2500 grams; a portion of this product, after the removal of some resinous matter, melted at 43—44°. The mother liquor from this fraction was then diluted with sufficient water to precipitate the whole of the acids remaining in solution, which separated as a somewhat oily cake; the latter was then subjected to pressure, and was thus separated into 1500 grams of solid acids, which, after purification, melted at 36—38°, and 950 grams of a light brown oil.

Identification of Palmitic Acid.

The 950 grams of oil obtained by expression, as stated above, were fractionally distilled, when practically the whole passed over between 210° and 235°/10 mm. A fraction which distilled between 210° and 220°/10 mm. was separated; it passed over as a slightly yellow oil, which, however, solidified on cooling. In order to remove some adhering oil, it was drained at the pump and finally on porous earthenware. The dry acid was then crystallised, first from methyl alcohol, then from acetone, when it melted at 62—63°, and finally from ethyl acetate, when its melting point remained unchanged. It was definitely shown to be palmitic acid by analysis and titration, by the estimation of silver in its silver salt, as also by the fact that it was optically inactive and behaved as a saturated compound towards bromine and permanganate.

Isolation of a New Unsaturated Acid, Chaulmoogric Acid, $C_{18}H_{32}O_2$.

In the course of the fractional crystallisation of the fatty acids (p. 845), the isolation of a large quantity of an individual substance, melting at 68°, was noted.

0·1416 gave 0·3976 CO_2 and 0·1460 H_2O. C = 76·6; H = 11·5.
0·1432 „ 0·4046 CO_2 „ 0·1500 H_2O. C = 77·0; H = 11·6.
0·1344 „ 0·3783 CO_2 „ 0·1388 H_2O. C = 76·8; H = 11·4.
$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent.

The silver salt was prepared from an alcoholic solution of the ammonium salt, and formed a white, amorphous precipitate, which was washed successively with water, alcohol, and ether.

0·1280 gave 0·0356 Ag. Ag = 27·8.
0·0884 „ 0·1804 CO_2, 0·0666 H_2O, and 0·0246 Ag.
C = 55·7; H = 8·4; Ag = 27·8.
$C_{18}H_{31}O_2Ag$ requires C = 55·8; H = 8·0; Ag = 27·9 per cent.

0·6914, in alcohol, required NaOH equivalent to 24·6 c.c. of a decinormal solution, and 0·8022 required 28·6 c.c., which are the calculated amounts for $C_{18}H_{32}O_2$.

It is thus quite evident that the acid melting at 68° has the formula $C_{18}H_{32}O_2$, and is isomeric with linolic acid, which belongs to the series $C_nH_{2n-4}O_2$. All the known acids of this series are unsaturated to the extent of two ethylenic linkings, or, in other words, combine directly with four atomic proportions of bromine or iodine. They are, therefore, all open chain, unsaturated acids. The acid melting at 68°, however, combines directly with only two atomic proportions of bromine or iodine.

0·7428 absorbed 0·6697 iodine. I = 90·1.

$C_{18}H_{32}O_2$, with one ethylenic linking, requires I = 90·6.

$C_{18}H_{32}O_2$, with two ethylenic linkings, requires I = 181·2 per cent.

This fact, together with some results recorded in the following paper, shows that this acid, although having the general formula $C_nH_{2n-4}O_2$, contains only one ethylenic linking; it, therefore, must necessarily contain a closed carbon ring. In view of this conclusion, it became clear that it represents a new substance, since no acid of an alicyclic nature has hitherto been isolated from the fats or oils. On account of the vernacular name of the oil from which it has been isolated, it has been decided to designate this new acid as *chaulmoogric acid.*

Another interesting character of the acid, which again differentiates it from any of the known acids of the same formula, is its optical activity.

A solution containing 3·892 grams in 100 c.c. of chloroform gave $\alpha_D + 2°11'$ in a 1 dcm. tube, whence $[\alpha]_D + 56°$.

Chaulmoogric acid, as compared with its known isomerides, is a very stable substance; it can be distilled without the slightest decomposition, and passes over at 247—248° (corr.)/20 mm. as a colourless oil, which soon solidifies to a solid, crystalline mass. The distilled acid was analysed.

0·1258 gave 0·3545 CO_2 and 0·1315 H_2O. C = 76·9; H = 11·6.

$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent.

Chaulmoogric acid is readily oxidised by cold potassium permanganate or nitric acid. It is also readily attacked by concentrated sulphuric acid, with much decomposition and the evolution of sulphur dioxide.

It is sparingly soluble in, and can readily be crystallised from, the usual organic solvents, with the exception of chloroform and ether, in which it is easily soluble even in the cold. It is also soluble in aqueous solutions of the alkalis, forming salts which have the character of soaps.

A number of the metallic salts of the acid have been prepared and analysed. They are of the types $C_{18}H_{31}O_2M'$, $(C_{18}H_{31}O_2)_2M''$, and $(C_{18}H_{31}O_2)_3M'''$ respectively, but in the case of the potassium salts an acid salt having the formula $C_{18}H_{31}O_2K,2C_{18}H_{32}O_2$ is formed, besides the normal salt, $C_{18}H_{31}O_2K$. Such acid potassium salts of monobasic acids are also known in the cases of palmitic and stearic acids.

The *ammonium* salt, $C_{18}H_{31}O_2\cdot NH_4$, crystallises from alcohol in pearly leaflets. On heating at 110° or on boiling its aqueous solution, it is readily dissociated into ammonia and chaulmoogric acid.

0·3907, on heating, lost 0·0237 NH_3. $NH_3 = 6·1$.

$C_{18}H_{35}O_2N$ requires $NH_3 = 5·7$ per cent.

The *normal potassium* salt, $C_{18}H_{31}O_2K$, was obtained as an amorphous powder by precipitation with ether from a strongly alkaline alcoholic solution.

0·3054 gave 0·0866 K_2SO_4. $K = 12·7$.

$C_{18}H_{31}O_2K$ requires $K = 12·3$ per cent.

The *acid potassium* salt, $C_{18}H_{31}O_2K,2C_{18}H_{32}O_2$, forms needles from a neutral aqueous solution.

0·2118 gave 0·0226 K_2SO_4. $K = 4·8$.

$C_{18}H_{31}O_2K,2C_{18}H_{32}O_2$ requires $K = 4·4$ per cent.

The *sodium* salt resembled the potassium salt, but was more difficult to prepare.

The *lithium* salt, $C_{18}H_{31}O_2Li$, prepared by boiling an alcoholic solution of the acid with lithium carbonate, forms fern-like crystals, which are fairly soluble in hot, but only slightly so in cold, dilute alcohol.

0·6886 gave 0·1316 Li_2SO_4. $Li = 2·4$.

$C_{18}H_{31}O_2Li$ requires $Li = 2·4$ per cent.

The following salts were all prepared from a warm alcoholic solution of the potassium salt by precipitation with a soluble salt of the respective metal.

The *calcium* salt, $(C_{18}H_{31}O_2)_2Ca$, *barium* salt, $(C_{18}H_{31}O_2)_2Ba$, and *strontium* salt, $(C_{18}H_{31}O_2)_2Sr$, are white, amorphous powders.

0·3136 gave 0·0664 $CaSO_4$. $Ca = 6·2$.
0·2842 „ 0·0920 $BaSO_4$. $Ba = 19·0$.
0·2856 „ 0·0792 $SrSO_4$. $Sr = 13·2$.

$C_{36}H_{62}O_4Ca$ requires 6·7 ; $C_{36}H_{62}O_4Ba$ requires 19·8 ;
$C_{36}H_{62}O_4Sr$ requires 13·6 per cent.

The *magnesium* salt, $(C_{18}H_{31}O_2)_2Mg,2H_2O$, separates in needles.

0·3028 lost, at 100°, 0·0178 H_2O and gave 0·0184 MgO. $H_2O = 5·9$; $Mg = 3·7$.

$C_{36}H_{62}O_4Mg,2H_2O$ requires $H_2O = 5·8$; $Mg = 3·9$ per cent.

The *zinc* salt, $(C_{18}H_{31}O_2)_2Zn$, forms small, colourless crystals.

0·3174 gave 0·0410 ZnO. $Zn = 10·4$.

$C_{36}H_{62}O_4Zn$ requires $Zn = 10·5$ per cent.

The *ferric* salt, $(C_{18}H_{31}O_2)_3Fe$, is a light brown, amorphous powder.

0·2282 gave 0·0204 Fe_2O_3. Fe = 6·3.
$C_{54}H_{93}O_6Fe$ requires Fe = 6·3 per cent.

The *manganous* salt, $(C_{18}H_{31}O_2)_2Mn$, is a nearly white, amorphous powder.

0·2550 gave 0·0318 Mn_3O_4. Mn = 9·0.
$C_{36}H_{62}O_4Mn$ requires Mn = 9·0 per cent.

The *lead* salt, $(C_{18}H_{31}O_2)_2Pb$, is a white, amorphous powder.

0·3066 gave 0·1226 $PbSO_4$. Pb = 27·3.
$C_{36}H_{62}O_4Pb$ requires Pb = 27·1 per cent.

The *copper* salt, $(C_{18}H_{31}O_2)_2Cu$, is a light green powder.

0·3936 gave 0·0490 CuO. Cu = 9·9.
$C_{36}H_{62}O_4Cu$ requires Cu = 10·2 per cent.

Intermediate Fractions obtained in the Separation of Palmitic and Chaulmoogric Acids (p. 845).

Fraction melting at 59—61°.—This fraction was found to boil between 230° and 240°/11—12 mm.

10·2 grams in 100 c.c. of chloroform gave a_D +2°9′ in a 50 mm. tube, whence $[a]_D$ +42·2°.

0·1032 gave 0·2868 CO_2 and 0·1062 H_2O. C = 75·7 ; H = 11·4.
0·0802 „ 0·2220 CO_2 „ 0·0814 H_2O. C = 75·5 ; H = 11·3.
$C_{18}H_{32}O_2$ requires C = 77·1 ; H = 11·4 per cent.
$C_{16}H_{32}O_2$ „ C = 75·0 ; H = 12·5 „
$C_{16}H_{28}O_2$ „ C = 76·2 ; H = 11·1 „
$C_{14}H_{24}O_2$ „ C = 75·0 ; H = 10·7 „

0·9244 required NaOH equivalent to 35·3 c.c. of a decinormal solution, instead of 33 c.c. or 36·1 c.c., the calculated amounts for $C_{18}H_{32}O_2$ or $C_{16}H_{32}O_2$ respectively.

0·6944 required 0·4673 iodine. I = 67·3.
$C_{18}H_{32}O_2$, with one ethylenic linking, requires I = 90·6.
$C_{16}H_{28}O_2$, „ „ „ „ I = 100·7 per cent.

From a consideration of these results, this fraction probably contains chaulmoogric and palmitic acids, together with an acid or acids of lower carbon content than C_{18}, and belonging to the series $C_nH_{2n-4}O_2$ with one ethylenic linking.

Fraction melting at 34—35°.—This fraction distilled between 218° and 225°/11—12 mm.

14·93 grams in 100 c.c. of chloroform gave α_D +3°5′ in a 50 mm. tube, whence $[\alpha]_D$ +41·5°.

0·0870 gave 0·2398 CO_2 and 0·0886 H_2O. C = 75·2 ; H = 11·3.
0·1006 ,, 0·2774 CO_2 ,, 0·1016 H_2O. C = 75·2 ; H = 11·2 per cent.

1·0014 required NaOH equivalent to 39 c.c. of a decinormal solution, which is the calculated amount for $C_{16}H_{32}O_2$.

0·6972 required 0·6163 iodine. I = 88·4 per cent.

From these data it is probable that this fraction consists largely of an acid or acids having the formula $C_{16}H_{28}O_2$ or $C_{14}H_{24}O_2$, belonging to the series $C_nH_{2n-4}O_2$ with one ethylenic linking.

Fraction melting at 43—44°.—This fraction distilled between 224° and 234°/11—12 mm.

12·66 grams in 100 c.c. of chloroform gave α_D +3°34′ in a 50 mm. tube, whence $[\alpha]_D$ +56·3°.

0·0884 gave 0·2430 CO_2 and 0·0884 H_2O. C = 75·0 ; H = 11·1.
0·1173 ,, 0·3243 CO_2 ,, 0·1172 H_2O. C = 75·4 ; H = 11·1 per cent.

1·0962 required NaOH equivalent to 42·6 c.c. of a decinormal solution, instead of 39·1 c.c. or 42·8 c.c., the calculated amounts for $C_{18}H_{32}O_2$ or $C_{16}H_{32}O_2$ respectively.

0·6948 required 0·6700 iodine. I = 96·4 per cent.

The probable composition of this fraction may be indicated by the remarks appended to the one preceding it.

Fraction melting at 36—38°.—This fraction distilled between 225° and 235°/11—12 mm.

11·6 grams in 100 c.c. of chloroform gave α_D +2°54′ in a 50 mm. tube, whence $[\alpha]_D$ +50°.

0·1060 gave 0·2922 CO_2 and 0·1054 H_2O. C = 75·2 ; H = 11·0.
0·1070 ,, 0·2940 CO_2 ,, 0·1054 H_2O. C = 74·9 ; H = 11·0 per cent.

1·0002 required NaOH equivalent to 37·5 c.c. of a decinormal solution, instead of 35·7 c.c. or 39 c.c., the calculated amounts for $C_{18}H_{32}O_2$ or $C_{16}H_{32}O_2$ respectively.

0·6942 required 0·6460 iodine. I = 93·1 per cent.

From these data, the composition of this fraction would appear to be essentially that of the preceding one.

The Oily Acid separated by Pressure.—This fraction distilled between 218° and 227°/10 mm. as an almost colourless oil, which, on cooling, formed a nearly solid cake melting at 20°.

14·14 grams in 100 c.c. of chloroform gave α_D +3°4′ in a 50 mm. tube, whence $[\alpha]_D$ +43·4°.

0·0820 gave 0·2302 CO_2 and 0·0826 H_2O. C = 76·6 ; H = 11·2.
0·0858 „ 0·2408 CO_2 „ 0·0864 H_2O. C = 76·5 ; H = 11·2 per cent.

0·9936 required NaOH equivalent to 37·6 c.c. of a decinormal solution, instead of 35·5 c.c. or 38·8 c.c., the calculated amounts for $C_{18}H_{32}O_2$ or $C_{16}H_{32}O_2$ respectively.

0·6984 required 0·8976 iodine. I = 128·5 per cent.

It has already been shown that palmitic acid is contained in this fraction (p. 849). The high percentage of iodine required indicates, however, that it contains a considerable proportion of an acid or acids of the series $C_nH_{2n-4}O_2$, but with two ethylenic linkings.

From the results of the examination of the foregoing intermediate fractions, it would thus appear that they contain, besides chaulmoogric acid and a small proportion of palmitic acid, some lower homologues of the former, of the series $C_nH_{2n-4}O_2$, on the one hand with a closed ring and one ethylenic linking, and on the other with two ethylenic linkings.

We cannot confirm the statement of Moss (*loc. cit.*) that undecyclic acid ("cocinic" acid) is a constituent of chaulmoogra oil, nor have we been able to isolate an individual acid which would correspond with hypogæic acid. From our experience in the separation of the acids of chaulmoogra oil, it may confidently be stated that the "gynocardic acid" of Moss, and of subsequent investigators, does not represent an individual substance.

We have prepared, and are at present investigating, the fatty oil from the seeds of *Gynocardia odorata* (R.Br.); it appears to be very different in character from that obtained from the seeds of *Taraktogenos Kurzii* (King), which we have proved to be identical with the chaulmoogra oil of commerce.

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