The constituents of the seeds of Hydnocarpus wightiana, Blume, and of Hydnocarpus anthelmintica, Pierre / by Frederick B. Power and Marmaduke Barrowcliff.

No. 54

THE CONSTITUENTS OF THE SEEDS OF HYDNOCARPUS WIGHTIANA, *Blume* AND OF HYDNOCARPUS ANTHELMINTICA, *Pierre*

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XCI.—*The Constituents of the Seeds of Hydnocarpus Wightiana and of Hydnocarpus anthelmintica. Isolation of a Homologue of Chaulmoogric Acid.*

By Frederick Belding Power and Marmaduke Barrowcliff.

In a previous paper (Trans., 1904, 85, 838), one of us, in conjunction with Mr. F. H. Gornall, gave an account of an investigation of chaulmoogra seeds (from *Taraktogenos Kurzii*, King), which afford the chaulmoogra oil of commerce. The fatty oil from the seeds was shown to consist chiefly of the glyceryl esters of members of a homologous series of acids of an entirely new type. The acids of this series have the general formula $C_nH_{2n-4}O_2$, but contain only one ethylenic linking, and therefore must necessarily possess an alicyclic

grouping; they are also characterised by their optical activity. One of these acids was isolated in a pure state, was shown to have the formula $C_{18}H_{32}O_2$, and was designated chaulmoogric acid (compare Power and Gornall, Trans., 1904, **85**, 851).

The fatty oils from the seeds of two species of *Hydnocarpus*, namely, *H. Wightiana* (Blume) and *H. anthelmintica* (Pierre), which belong to the same natural order as *Taraktogenos*, have long been used in Western India and in China respectively for the same medicinal purposes for which chaulmoogra oil is employed.

Hydnocarpus Wightiana (Blume) is the designation of a tree indigenous to the Western Peninsula of India, from South Concan to Travancore. The oil from the seeds has been brought to the notice of Europeans as a substitute for chaulmoogra oil, and has been used in the Bombay Presidency with satisfactory results. The seeds are not an article of commerce.

Hydnocarpus anthelmintica (Pierre) is a tree indigenous to Siam, the seeds of which are exported to China under the name of "Lukrabo," and are known in the latter country as "Ta-fung-tsze" (compare *Pharmacographia Indica*, Vol. I, pp. 146, 148, and *Pharm. J.*, 1900, **64**, 522).

In view of the interesting facts elicited by the investigation of chaulmoogra seeds (*loc. cit.*) and the considerations referred to, it seemed desirable that the seeds of the above-mentioned two species of *Hydnocarpus* should also be chemically examined, more especially with regard to the constituents of their fatty oils, and the present communication embodies the results which have been obtained.

It may be briefly stated that the fatty oils from the seeds of *H. Wightiana* (Blume) and of *H. anthelmintica* (Pierre) very closely resemble chaulmoogra oil both in their physical characters and in their chemical composition. The acids obtained from the respective Hydnocarpus oils consist chiefly of chaulmoogric acid and a lower homologue of the same series, the latter having been isolated from both oils and now also from chaulmoogra oil. This new acid has the formula $C_{16}H_{28}O_2$, and is designated *hydnocarpic acid*.

Hydnocarpic acid crystallises from alcohol in glistening leaflets, melts at 60°, and has $[\alpha]_D$ + 68° in chloroform solution. Like chaulmoogric acid, it contains only one ethylenic linking, and therefore, in consideration of its formula $C_{16}H_{28}O_2(C_nH_{2n-4}O_2)$, must possess an alicyclic grouping.

The seeds of the two species of *Hydnocarpus*, like chaulmoogra seeds, contain smaller amounts of other substances, but these are of minor interest as compared with that attaching to chaulmoogric and hydnocarpic acids, and the record of their identification will be found in the experimental section of the paper.

Experimental.

I. *The Constituents of the Seeds of Hydnocarpus Wightiana (Blume).*

The seeds of *Hydnocarpus Wightiana* not being an article of commerce, a quantity of them was obtained for us in India, and we have further assured ourselves of their genuineness.

Immediately on their arrival, several of the seeds were crushed, brought into contact with water, and the mixture allowed to remain in a corked flask for some hours. As no hydrogen cyanide was developed, it was evident that they contained no cyanogenetic glucoside at the time of their examination by us, although such a substance may have existed in them at an earlier period (compare Power and Gornall, Trans., 1904, **85**, 840).

In order to obtain the fatty oil, the kernels, which represented 75 per cent. of the weight of the seeds, were subjected to powerful hydraulic pressure. This treatment afforded an amount of a fatty oil and of a "press-cake" equivalent, respectively, to 32·4 and 35·4 per cent. of the weight of the entire seeds. By completely extracting the total powdered seed with ether, 41·2 per cent. of oil was obtained.

The Fatty Oil.

The oil from the seeds of *Hydnocarpus Wightiana*, like true chaulmoogra oil (from *Taraktogenos Kurzii*, King), is, at the ordinary temperature, a soft solid, having a faintly yellow colour and a characteristic odour. It gave the following values :

	Expressed oil.	Oil extracted by ether.
Melting point.....	22—23°	22—23°
Specific gravity	0·958 at 25°	0·959 at 25°
$[\alpha]_D$ in chloroform	+57·7°	+56·2°
Acid value	3·8	7·4
Saponification value	207·0	207·0
Iodine value	101·3	102·5

Hydrolysis of the Fatty Oil.

One hundred grams of the oil were hydrolysed with alcoholic potassium hydroxide, the alcohol removed, and the residue mixed with sand, dried, and extracted with light petroleum. The latter yielded a small amount of an oily residue ; this was dissolved in warm alcohol, and on cooling the solution a substance separated, which, on recrys-

tallisation from ethyl alcohol, formed glistening needles melting at 132—133°.

0·0266 gave 0·0812 CO_2 and 0·0292 H_2O. C = 83·3 ; H = 12·2.
$C_{26}H_{44}O$ requires C = 83·9 ; H = 11·8 per cent.

The colour reactions of this substance confirmed its identity as phytosterol.

The Fatty Acids.

The potassium salts obtained by the above hydrolysis were dissolved in water, the liquid acidified with sulphuric acid, and the liberated fatty acids taken up by ether. The ethereal solution was then washed, dried, and the ether removed, the last traces of the latter being eliminated by heating the residual oil at 100° for some time. On cooling, a hard, white cake was obtained, representing the total fatty acids. These gave the following values: melting point, 41—44°; $[\alpha]_D$ in chloroform + 60·4° ; acid value, 214·0 ; iodine value, 106·3.

For the investigation of the mixture of fatty acids, 1000 grams of the fat were hydrolysed, the aqueous solution of the potassium salts acidified, and the solid cake of acids collected, washed with water, drained at the pump, and then dried between filter paper. The aqueous filtrate from the fatty acids was distilled in steam, and from the acid distillate a barium salt was prepared. The latter was very small in amount and consisted of the salts of acetic and butyric acids.

The solid mixture of acids was fractionally crystallised from alcohol. The first crystalline crop which separated from the alcoholic solution of the whole of the acids from the 1000 grams of fat weighed 200 grams and melted at 46—48°. On further crystallisation, however, from alcohol and from ethyl acetate, it was obtained in the form of glistening leaflets having the constant melting point of 67—68° and giving the following results on analysis:

0·0792 gave 0·2230 CO_2 and 0·0810 H_2O. C = 76·8 ; H = 11·4.
0·1030 „ 0·2904 CO_2 „ 0·1056 H_2O. C = 76·9 ; H = 11·4.
$C_{18}H_{32}O_2$ requires C = 77·1 ; H = 11·4 per cent.
0·1412 absorbed 0·1270 iodine. I = 90·0.
$C_{18}H_{32}O_2$, with one ethylenic linking, requires I = 90·6 per cent.
1·2032, in alcohol, required NaOH equivalent to 42·7 c.c. of a decinormal solution, which is the calculated amount for $C_{18}H_{32}O_2$.

A solution of 1·8127 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D + 4°15′, whence $[\alpha]_D$ + 58·6°.

It was thus shown that this acid melting at 67—68° was in all respects identical with chaulmoogric acid, first obtained by Power and Gornall (*loc. cit.*) from chaulmoogra oil (from the seeds of *Taraktogenos Kurzii*, King).

The alcoholic mother liquor from the above-mentioned first crystalline crop afforded, by successive concentrations, several further crops of crystals, and then a final mother liquor. The latter, although still containing a considerable amount of substance in solution, deposited nothing further of a crystalline character. The treatment of this mother liquor is subsequently described.

The further crops of crystalline acids were then subjected to a systematic and extended process of fractional crystallisation. All the fractions so obtained were found to melt approximately at 48—50°, but when separating from solution they presented an appearance which, although identical for all the fractions, did not satisfy us that we were dealing with an individual acid. Moreover, evidence of a quantitative nature indicated that the above fractions consisted of a molecular mixture of chaulmoogric acid, $C_{18}H_{32}O_2$, and a homologous acid having the formula $C_{16}H_{28}O_2$. This supposition was subsequently verified, for it has been possible to separate these acids by resorting to a process of fractional precipitation and crystallisation of their barium salts.

Isolation of a Homologue of Chaulmoogric Acid—Hydnocarpic Acid, $C_{16}H_{28}O_2$.

Two hundred and fifty grams of the above fractions melting at 48—50° were dissolved in 1 litre of alcohol. To this solution there was added a solution of 25 grams of barium acetate in the smallest possible quantity of water, the amount of barium acetate thus employed being sufficient to convert one-fifth of the total weight of the fatty acids into barium salts. The fraction of barium salts, which was at once precipitated as a sticky mass, was then dissolved by heating the liquid. On cooling, it again separated, but in a crystalline form ; it was collected at the pump and washed with alcohol. The mother liquor from this first fraction of barium salts was then treated with another 25 grams of barium acetate, and a second fraction of barium salts obtained in precisely the same manner as was the first. The whole process was then twice repeated, and the remaining one-fifth of the acids, not being converted into barium salts, was obtained by removing the solvent.

The four fractions of barium salts and the acids from the mother liquor from the fourth fraction of these salts were respectively digested with dilute hydrochloric acid. The regenerated acids were then dissolved in ether, the ethereal solutions washed, dried, the ether removed, and the residues recrystallised from alcohol. The melting points of the several fractions of acids, placed in the order in which the latter were obtained, were as follows: (1) 53—55°; (2) 60—62°; (3)

46—47°; (4) 53—55°; (5) 56—58°. Fraction (2), on recrystallisation from alcohol, gave chaulmoogric acid melting at 67—68°. Fractions (4) and (5) were combined and recrystallised from alcohol. The recrystallised acid then melted at 59—60°, was in the form of lustrous leaflets, and, on further crystallisation from alcohol or ethyl acetate, its melting point remained unchanged.

0·1018 gave 0·2833 CO_2 and 0·1022 H_2O. C = 75·9; H = 11·2.
0·1056 „ 0·2945 CO_2 „ 0·1052 H_2O. C = 76·1; H = 11·1.
$C_{16}H_{28}O_2$ requires C = 76·2; H = 11·1 per cent.

0·3749 required NaOH equivalent to 14·8 c.c. of a decinormal solution, which is the calculated amount for $C_{16}H_{28}O_2$.

0·2608 absorbed 0·2612 iodine. I = 100·2.

$C_{16}H_{28}O_2$, with one ethylenic linking, requires I = 100·7 per cent.

The *silver* salt was prepared and analysed:

0·2724 gave 0·0815 Ag. Ag = 29·9.
0·1700 „ 0·3296 CO_2, 0·1138 H_2O, and 0·0510 Ag.
C = 52·9; H = 7·4; Ag = 30·0.
$C_{16}H_{27}O_2Ag$ requires C = 53·5; H = 7·5; Ag = 30·1 per cent.

It was thus shown that this acid, melting at 59—60°, has the formula $C_{16}H_{28}O_2$, contains only one ethylenic linking, and therefore must possess a closed carbon ring. In other words, it is a lower homologue of chaulmoogric acid, and belongs to the same type as the latter. We have designated this new acid *hydnocarpic acid.*

Hydnocarpic acid, like chaulmoogric acid, is optically active.

A solution of 1·3063 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D +3°34′, whence $[\alpha]_D$ +68·1°.

Hydnocarpic acid is only sparingly soluble in the cold in the usual organic solvents, with the exception of chloroform, in which it is easily soluble. An aqueous solution of its sodium salt at once decolorises permanganate in the cold. Like chaulmoogric acid, it remains unattacked by fused potassium hydroxide, even at 250°. The following derivatives of the acid were prepared and characterised.

Methyl Hydnocarpate, $C_{15}H_{27}\cdot CO_2Me$.

Five grams of hydnocarpic acid were dissolved in 25 c.c. of methyl alcohol and 5 grams of sulphuric acid slowly added, when the ester soon separated as an oil. After the mixture had been allowed to stand for some hours, water was added, the oil taken up with ether, the ethereal solution washed with sodium carbonate, then with water, dried, the ether removed, and the ester distilled under diminished pressure.

Methyl hydnocarpate boils at 200—203° (corr.) under 19 mm. pressure, and is a colourless oil, which, however, solidifies when cooled, forming a mass of colourless crystals, melting again at 8°.

0·0973 gave 0·2739 CO_2 and 0·0988 H_2O. C = 76·8 ; H = 11·3.
$C_{17}H_{30}O_2$ requires C = 76·7 ; H = 11·3 per cent.

A solution of 0·9818 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube $\alpha_D + 2°27'$, whence $[\alpha]_D + 62·4°$.

Ethyl Hydnocarpate, $C_{15}H_{27}\cdot CO_2Et$.

This substance was prepared in the same manner as the methyl ester ; it boils at 211° (corr.) under 19 mm. pressure, and is a colourless oil.

0·0955 gave 0·2689 CO_2 and 0·0976 H_2O. C = 76·8 ; H = 11·4.
$C_{18}H_{32}O_2$ requires C = 77·1 ; H = 11·4 per cent.

A solution of 0·5087 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube $\alpha_D + 1°3'$, whence $[\alpha]_D + 51·6°$.

Hydnocarpamide, $C_{15}H_{27}\cdot CO\cdot NH_2$.

Five grams of the acid were warmed with a slight excess of phosphorus trichloride. The acid chloride was then dissolved in ether and this solution slowly added to 50 c.c. of concentrated ammonia solution, cooled to 0°. The solid amide, which was at once formed, was collected, washed with water, with dilute sodium hydroxide, again with water, and then recrystallised from ethyl alcohol.

Hydnocarpamide separates from alcohol in clusters of fine, colourless needles which melt at 112—113°.

0·0995 gave 0·2787 CO_2 and 0·1054 H_2O. C = 76·4 ; H = 11·8.
$C_{16}H_{29}ON$ requires C = 76·5 ; H = 11·6 per cent.

A solution of 0·6947 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube $\alpha_D + 1°57'$ at 30°, whence $[\alpha]_D^{30°} + 70·2°$.

The Alcoholic Mother Liquor from Chaulmoogric and Hydnocarpic Acids.

It was stated on p. 888 that after separating from the alcoholic solution of the fatty acids several crystalline crops, which subsequently afforded chaulmoogric and hydnocarpic acids, there remained a final mother liquor which deposited nothing further in a crystalline form, although still containing an appreciable quantity of acids in solution. On the addition of water, these acids separated in an oily

condition. They were dissolved in ether, the ethereal solution washed, dried, and the ether removed. The residual oil, on standing, deposited a small amount of solid acids. The latter were collected at the pump, drained on porous earthenware, and distilled, when the whole passed over at 220—225° under 20 mm. pressure.

0·1327 gave 0·3690 CO_2 and 0·1302 H_2O. C = 75·9 ; H = 10·9.
$C_{18}H_{32}O_2$ requires C = 77·1 ; H = 11·4 per cent.
$C_{16}H_{28}O_2$,, C = 76·2 ; H = 11·1 ,,
$C_{14}H_{24}O_2$,, C = 75·0 ; H = 10·7 ,,

0·2456 absorbed 0·2638 iodine. I = 107·4.
$C_{18}H_{32}O_2$, with one ethylenic linking, requires I = 90·6 per cent.
$C_{16}H_{28}O_2$, ,, ,, ,, ,, ,, I = 100·7 ,,
$C_{14}H_{24}O_2$, ,, ,, ,, ,, ,, I = 113·4 ,,

A solution of 0·8902 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube $\alpha_D + 2°$, whence $[\alpha]_D + 56·1°$.

The solid fraction, which was obviously a mixture, since it could not be crystallised, would appear to consist of chaulmoogric and hydnocarpic acids, together with a still lower homologue of the same series having the formula $C_{14}H_{24}O_2$.

The filtrate from the above solid fraction amounted to 38 grams. It was distilled under 20 mm. pressure, and the following fractions were collected.

Fraction boiling at 220—225°/20 *mm.*—This was at first wholly an oil, but after a time an amount of solid acids separated.

0·2408 absorbed 0·3109 iodine. I = 129·1 per cent.

Its specific rotatory power in chloroform was $[\alpha]_D + 41·9°$.

Fraction boiling at 225—230°/20 *mm.*—This was similar to the preceding fraction.

0·3673 absorbed 0·4815 iodine. I = 131·1 per cent.

Its specific rotatory power in chloroform was $[\alpha]_D + 46·6°$.

Fraction boiling at 230—235°/20 *mm.*—This was the largest of these fractions, and on standing it also partly solidified.

0·1193 gave 0·3401 CO_2 and 0·1212 H_2O. C = 76·6 ; H = 11·0.
0·2330 absorbed 0·3279 iodine. I = 140·7 per cent.

Its specific rotatory power in chloroform was $[\alpha]_D + 50·4°$.

These three fractions, in view of their high specific rotatory powers, would still appear to contain a large proportion of the members of the chaulmoogric acid series, but their percentage iodine-absorption values, which are appreciably higher than that required for an acid of the

formula $C_{14}H_{24}O_2$ of the latter series, indicate that they also contain an acid or acids belonging to the linolic or linolenic acid series.

There was no evidence of the occurrence of palmitic acid in the fatty oil from *Hydnocarpus Wightiana*, and in this respect it differs from the oil from *Taraktogenos Kurzii*, which contains an appreciable amount of this acid.

Examination of the "Press-cake."

The "press-cake," which remained after the greater part of the fatty oil had been removed from the seeds by expression, was completely extracted with hot alcohol. The greater part of the alcohol was then removed, when a brown, pasty solid was obtained. Two kilograms of the latter were distilled in steam, and the distillate, which contained a small amount of suspended oil, was neutralised with baryta water and extracted with ether. On removing the ether, a limpid, odorous oil was obtained, but which was too small in amount to admit of further examination. The aqueous liquid afforded a very small quantity of a barium salt, which was found to consist of a mixture of barium formate and butyrate. The liquid in the steam-distillation flask consisted of two layers, one being a fatty oil and the other a dark aqueous liquid. On cooling, the fatty oil solidified. The aqueous liquid was separated by means of a linen strainer, and was quite free from any suspended oil.* It was digested with animal charcoal and concentrated to a syrupy consistence, but nothing crystalline separated, even on long standing. It contained a large amount of *i*-glucose, for it readily afforded a phenylglucosazone melting at 216°, and also much proteid matter.

Isolation of a Hydrolytic Enzyme.

A portion of the "press-cake" was digested with water and the filtered liquid mixed with twice its volume of alcohol. After some hours, the precipitate was collected, washed with alcohol, dried over sulphuric acid, and reduced to a powder. The yield of this substance was about 2 per cent. of the weight of the "press-cake." It readily effected the hydrolysis of both amygdalin and potassium myronate.

* In the examination of the "press-cake" from chaulmoogra seeds (Power and Gornall, *loc. cit.*, p. 842), the aqueous liquid which passed through the strainer contained an oil in suspension. It was stated that the latter was hydrolysed with potassium hydroxide, and that, on subsequently extracting with ether, an oil was obtained. The latter was regarded as a substance which could be neither an acid nor an ester. We have since found that, inadvertently, an insufficient amount o potassium hydroxide was employed, and that, therefore, the hydrolysis was no quite complete. The oil which was thus obtained has been ascertained to consist of ethyl esters, formed from the fatty acids during the extraction of the "press-cake' with alcohol.

II. *The Constituents of the Seeds of Hydnocarpus anthelmintica (Pierre).*

A large quantity of these seeds was obtained for us in Siam, and their genuineness verified.

When the kernels from 20 grams of the seeds were crushed and mixed with water, a distinct odour of hydrogen cyanide was soon developed, thus indicating that they contained a cyanogenetic glucoside. An attempt was accordingly made to isolate this substance from 2 kilograms of the seeds, employing the same method as was successful in obtaining gynocardin from the seeds of *Gynocardia odorata*, R.Br. (Power and Lees, Trans., 1905, **87**, 352). The amount of glucoside present was, however, very small, and nothing crystalline was obtained.

The seeds were first divested of their shells, which represented 68·8 per cent. of their weight. The kernels were then subjected to hydraulic pressure, and afforded an amount of a fatty oil and of a "press-cake" equivalent, respectively, to 16·3 and 15 per cent. of the entire seeds. By completely extracting the total powdered seed with ether, 17·6 per cent. of oil was obtained.

The Fatty Oil.

The oil from the seeds of *Hydnocarpus anthelmintica* is, at the ordinary temperature, a nearly colourless, firm solid, having the same characteristic odour as is possessed by both chaulmoogra oil and that from the seeds of *H. Wightiana*. Its values were determined with the following results:

	Expressed oil.	Oil extracted by ether.
Melting point.....	24—25°	23—24°
Specific gravity	0·953 at 25°	0·952 at 25°
$[\alpha]_D$ in chloroform	+52·5°	+51°
Acid value	7·5	8·1
Saponification value ...	212·0	208·0
Iodine value	86·4	82·5

Hydrolysis of the Fatty Oil.

One hundred grams of the oil were hydrolysed with alcoholic potassium hydroxide, and the product extracted with light petroleum in the manner described on p. 886. The residue from the petroleum was exceedingly small in amount. After several crystallisations from alcohol, it was obtained in the form of glistening crystals melting at 132—133°, and was identical with the phytosterol obtained from the seeds of *Hydnocarpus Wightiana*.

The Fatty Acids.

From the potassium salts afforded by the above hydrolysis, the mixture of total fatty acids was obtained in the same manner as described on p. 887. It formed a hard, white solid and gave the following values: melting point, 42—43°; $[\alpha]_D$ in chloroform, +53·6°; acid value, 202·5; iodine value, 87·8.

For the identification of the constituents of this mixture of acids 1000 grams of the fat were hydrolysed with alcoholic potassium hydroxide. The aqueous solution of the potassium salts was acidified, the resulting cake of solid acids separated and washed, and the filtrate from the latter distilled in a current of steam. From the acid distillate, a barium salt was prepared, which was very small in amount, and was found to consist of a mixture of barium formate and acetate.

The solid mixture of acids, weighing about 850 grams, was fractionally crystallised from alcohol, just as in the case of the acids from *Hydnocarpus Wightiana*, and a quantity of a pure acid melting at 68° was thus obtained. This proved to be chaulmoogric acid.

0·1168 gave 0·3304 CO_2 and 0·1202 H_2O. C = 77·1; H = 11·5.
$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent.

A solution of 1·2014 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D +2°52′, whence $[\alpha]_D$ +59·5°.

The alcoholic mother liquor from the chaulmoogric acid afforded a quantity of a substance melting at about 48°, which was apparently identical with the molecular mixture of chaulmoogric and hydnocarpic acids obtained by the crystallisation of the acids from *Hydnocarpus Wightiana* (p. 888). Just as in the latter instance, these two acids were separated by fractionally precipitating and crystallising their barium salts. The hydnocarpic acid thus obtained melted at 59—60°.

0·1330 gave 0·3698 CO_2 and 0·1336 H_2O. C = 75·9; H = 11·2.
0·1224 „ 0·3405 CO_2 „ 0·1230 H_2O. C = 75·9; H = 11·2.
$C_{16}H_{28}O_2$ requires C = 76·2; H = 11·1 per cent.

0·2329 absorbed 0·2336 iodine. I = 100·3.
$C_{16}H_{28}O_2$, with one ethylenic linking, requires I = 100·7 per cent.

A solution of 0·68 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D +1°51′, whence $[\alpha]_D$ +68°.

The alcoholic mother liquor from the mixture of chaulmoogric and hydnocarpic acids, which deposited nothing further of a crystalline character, was diluted with water. The resulting oily mixture of acids was dissolved in ether, the ethereal solution washed, dried, and the

ether removed. The residual oil was then distilled under diminished pressure, when it passed over between 214° and 234°/12 mm., and amounted to 40 grams. It was converted into lead salts by dissolving in alcohol and adding a slight excess of lead acetate also dissolved in alcohol. The solution was then evaporated, mixed with sand, the mass dried, and fractionally extracted with dry ether in a Soxhlet apparatus. Two fractions of lead salts soluble in ether were thus obtained. The acids regenerated from the first fraction, on distillation, passed over principally at 221—226°/12 mm. The distilled fraction had the specific rotatory power $[\alpha]_D$ +34·1°, and a percentage iodine-absorption value of 92·4. When treated with mercurous nitrate, it afforded elaidic acid, which proved the presence of oleic acid.

The second fraction of lead salt was crystalline, and was found to consist chiefly of lead hydnocarpate.

The lead salt insoluble in ether and remaining in the Soxhlet apparatus was decomposed, and the regenerated acid, which was solid, crystallised from alcohol. It was finally obtained in needles melting at 60°, was shown to be a saturated acid, and was, in fact, palmitic acid.

0·0953 gave 0·2609 CO_2 and 0·1060 H_2O. C = 74·7 ; H = 12·4.
$C_{16}H_{32}O_2$ requires C = 75·0 ; H = 12·5 per cent.

The "press-cake" was extracted with alcohol, and the alcoholic extract examined in the same manner as that obtained from the seeds of *H. Wightiana*. It afforded a very small amount of acids volatile in steam, which were recognised as formic, acetic, and butyric acids. It also contained much inactive glucose and proteid substances.

The seeds of *H. anthelmintica* afforded, furthermore, 0·3 per cent. of a hydrolytic enzyme, which was isolated in the usual manner; it hydrolyses amygdalin, but does not act on potassium myronate.

Isolation of Hydnocarpic Acid from Chaulmoogra Oil (*from Taraktogenos Kurzii*, King).

During the investigation of chaulmoogra seeds (Power and Gornall, *loc. cit.*), it was shown that, after the removal of the chaulmoogric acid by crystallisation of the total fatty acids from alcohol, several fractions were obtained, the quantitative examination of which indicated the presence of a lower homologue of chaulmoogric acid. In view of the isolation of hydnocarpic acid from the two sources previously mentioned in this paper, it seemed desirable to attempt to isolate this acid from the fatty oil from *Taraktogenos* seeds.

A quantity of the total fatty acids was therefore fractionally crystallised from alcohol, and a large amount of chaulmoogric acid separated

The mother liquor from the latter acid afforded a large fraction consisting of a pasty solid which could not be crystallised. It was found, however, that by washing with cold alcohol the acids of an oily character were removed, and that the undissolved portion could then be readily crystallised by dissolving in warm alcohol. A large fraction melting at 46—48° was thus obtained, which was apparently identical with the molecular mixture of chaulmoogric and hydnocarpic acids obtained from *Hydnocarpus Wightiana* and *H. anthelmintica*. By fractional precipitation with barium acetate, the two acids were readily separated, and hydnocarpic acid, melting at 59—60°, definitely identified as a constituent of the fatty oil of *Taraktogenos* seeds.

0·1221 gave 0·3405 CO_2 and 0·1222 H_2O. C = 76·1 ; H = 11·1.
$C_{16}H_{28}O_2$ requires C = 76·2 ; H = 11·1 per cent.

0·1346 absorbed 0·1338 iodine. I = 99·4.
$C_{16}H_{28}O_2$, with one ethylenic linking, requires I = 100·7 per cent.

A solution of 1·2652 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D +3°26′, whence $[\alpha]_D$ +67·8°.

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