No. 55

THE CONSTITUENTS OF THE SEEDS

OF

GYNOCARDIA ODORATA, *R.Br.*

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AND

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THE WELLCOME CHEMICAL RESEARCH LABORATORIES

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TITLES OF PUBLISHED PAPERS FROM
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XCII.—*The Constituents of the Seeds of Gynocardia Odorata.*

By Frederick Belding Power and Marmaduke Barrowcliff.

Prior to the year 1900 it was generally believed that the "chaulmoogra oil" of commerce was obtained from the seeds of *Gynocardia odorata* (R. Br.). More recently, however, it has been recorded by Mr. E. M. Holmes (*Pharm. J.*, 1900, **64**, 522; 1901, **66**, 596), on the authority of Dr. Prain, Director of the Botanic Survey of India, that chaulmoogra oil is afforded by the seeds of *Taraktogenos Kurzii* (King), these seeds having evidently been wrongly referred to the genus *Gynocardia*. The results obtained by one of us and Mr. F. H. Gornall (Trans., 1904, **85**, 838) in an investigation of the oil from authentic seeds of *Taraktogenos Kurzii* are in accordance with the above observation, for it was proved that the latter oil is identical in its physical characters and in composition with the chaulmoogra oil of commerce.

We are now, moreover, in a position to state conclusively that the oil which has long been known in European commerce as "chaulmoogra oil," and sometimes described under the synonym of "gynocardia oil," has never been obtained from the seeds of *Gynocardia odorata*, for whereas chaulmoogra oil at the ordinary temperature is a solid (m. p. 22—23°), the oil from the seeds of *Gynocardia odorata* is a liquid. Furthermore, chaulmoogra oil is optically active and consists chiefly of the glyceryl esters of members of the chaulmoogric acid series, whereas the oil from gynocardia seeds is optically inactive and contains neither chaulmoogric acid nor its homologues.

The present investigation has shown that gynocardia oil consists of the glyceryl esters of the following acids: (1) linolic acid, or isomerides of the same series, constituting the largest proportion of the oil; (2) palmitic acid, in considerable amount; (3) linolenic and *iso*linolenic acids, the latter preponderating; and (4) oleic acid, in relatively small amount.

In addition to the fatty oil, gynocardia seeds contain, as has previously been shown (Power and Lees, this vol., p. 349), 5 per cent. of a crystalline glucoside, gynocardin, $C_{13}H_{19}O_9N,1\frac{1}{2}H_2O$, and a hydrolytic enzyme, gynocardase.

Experimental.

The seeds of *Gynocardia odorata* are not collected for commercial purposes, and some difficulty was experienced in obtaining them. Through the kindness, however, of Mr. David Hooper, Curator of the Indian Museum, Calcutta, it has been possible for us to procure a quantity of these seeds sufficient for a complete investigation of their constituents.

According to a private communication from Mr. Hooper, the recognised habitats of *Gynocardia odorata* are Sikkim, Assam, and Chittagong in Bengal, and he also informs us that in Assam the oil is sometimes expressed from the seeds by the natives.

The seeds employed in this investigation were collected in Sylhet, Assam, and their genuineness confirmed by Surgeon-Major Prain, Director of the Botanic Survey of India, by the Reporter on Economic Products to the Government of India, and also by Mr. E. M. Holmes, F.L.S., of London.

On divesting the seeds of their shells it was found that the latter represented 37 per cent. of their weight. The kernels, when subjected to hydraulic pressure, afforded an amount of fatty oil and of a "press-cake" equivalent, respectively, to 19·5 and 40 per cent. of the weight of the entire seed. By extracting the total powdered seed with ether, 27·2 per cent. of oil was obtained.

The Fatty Oil.

The fatty oil from the seeds of *Gynocardia odorata* is, at the ordinary temperature, a light yellow liquid, having an odour resembling that of linseed oil. It is optically inactive. The expressed oil, and that extracted from the seeds by ether, gave the following values respectively:

	Expressed oil.	Oil extracted by ether.
Specific gravity	0·925 at 25°	0·927 at 25°
Acid value	4·9	5·0
Saponification value......	197·0	199·6
Iodine value	152·8	152·0

Hydrolysis of the Fatty Oil.

One hundred grams of the fatty oil were hydrolysed with alcoholic sodium hydroxide, the alcohol removed, and the residue mixed with sand, dried, and extracted with light petroleum. The latter removed a very small amount of a substance which, after crystallisation from alcohol, melted at 133°, and proved to be phytosterol.

The Fatty Acids.

The sodium 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 for some time at 100°. The total mixed fatty acids thus obtained, which partially solidified on standing at the ordinary temperature, gave an acid value of 199·8, and an iodine value of 162·6.

In order to investigate the mixture of fatty acids, 500 grams of the fatty oil were hydrolysed, the acids liberated, and the portion volatile in steam removed. The latter consisted of very small amounts of formic and acetic acids. The non-volatile acids were separated from the aqueous liquid and allowed to stand, when a considerable amount of a crystalline substance was deposited. The latter, which was collected at the pump, amounted to 60 grams; it was dissolved in alcohol and converted into its lithium salt in three successive fractions, each of which, after precipitation, was redissolved by heat, allowed to crystallise, the acid regenerated, and then crystallised from alcohol. The first fraction of acid melted at 60—61°, the second at

59—60°, and the third at 59—61°. On further crystallisation of the first fraction it melted at 62°, and gave on analysis the following figures:

0·1086 gave 0·2991 CO_2 and 0·1220 H_2O. C = 75·1; H = 12·5.
$C_{16}H_{32}O_2$ requires C = 75·0; H = 12·5 per cent.

The solid acid which separated from the total fatty acids was thus shown to be palmitic acid.

The high iodine-absorption value (162·6) of the total fatty acids indicated the presence of linolic acid or acids of the same series, and, taking into consideration the large amount of palmitic acid isolated, also of acids of the linolenic series. For the identification of these acids the method was employed which depends on oxidation with permanganate, and the separation of the corresponding hydroxy-acids (compare Lewkowitsch's *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i, pp. 360—363).

Sixty grams of the oily acids, from which the large amount of palmitic acid had been removed as described above, were therefore oxidised with potassium permanganate, and the following products isolated:

(1) A crystalline acid, melting at 133°.

0·0747 gave 0·1862 CO_2 and 0·0773 H_2O. C = 68·0; H = 11·5.
$C_{18}H_{36}O_4$ requires C = 68·3; H = 11·4 per cent.

This product was thus identified as dihydroxystearic acid, and its formation proved the presence of oleic acid in the fatty oil.

(2) A crystalline mixture, melting at 156—159°.

0·1158 gave 0·2624 CO_2 and 0·1077 H_2O. C = 61·8; H = 10·3.
$C_{18}H_{36}O_6$ requires C = 62·1; H = 10·3 per cent.

This evidently consisted of isomeric tetrahydroxystearic acids, which could not be readily separated. They represented the chief product of the oxidation, and their formation would appear to prove the presence in the fatty oil of isomeric acids of the linolic series.

(3) A crystalline acid melting at 171°.

0·1010 gave 0·2100 CO_2 and 0·0866 H_2O. C = 56·7; H = 9·5.
$C_{18}H_{36}O_8$ requires C = 56·8; H = 9·5 per cent.

This acid was therefore *iso*linusic acid, a hexahydroxystearic acid, and its formation proved the occurrence of *iso*linolenic acid in the fatty oil.

(4) A very small amount of a mixture of acids melting considerably higher than *iso*linusic acid. This, in all probability, contained linusic acid (m. p. 203—205°), the hexahydroxystearic acid derived from

linolenic acid. The presence of the latter acid in the fatty oil was, however, definitely established by the formation of its crystalline hexabromide, which melted at 180—181°.

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