

THE FATTY OIL FROM THE SEEDS OF *BAUHINIA* *VARIEGATA*, LINN.

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The oil from the seeds of *Bauhinia variegata* Linn, consists of the glycerides of myristic, palmitic, stearic, lignoceric, oleic and linoleic acids together with the phytosterol, sitosterol, commonly found in the vegetable fats.

Bauhinia variegata Linn, known as *Kachnar* in Hindi, is a moderate sized deciduous tree (N. O. *Leguminosæ*) of the sub-Himalayan tract from Indus eastward. It is often cultivated both as an ornamental tree and for its flowers which are eaten as vegetables. The pods are 6"-12" by $\frac{1}{4}$ "-1" with 10-15 seeds which contain the fatty oil.

Fatty oils of the allied species *B. esculenta* (Bray, *Analyst.*, 1921, 46, 401) and *B. purpurea* (Kafuku and Hata, *J. Chem. Soc. Japan*, 1934, 55, 369) were worked for their physical and chemical constants and *B. purpurea* oil was shown to consist of the glycerides of myristic, palmitic, stearic, archidic, oleic and linoleic acids. The constituents of the oil from the seeds of *B. variegata* are now reported for the first time

EXPERIMENTAL.

The seeds of *B. variegata* were collected locally at New Forest, Dehra Dun. They consisted of 20% of endocarp and 80% of kernel which yielded 16.5% of a pale yellow fatty oil when extracted with petroleum ether and 6.1% of it when expressed (hot expression) in a hydraulic press. The constants given below are for the sample of the oil obtained by hot expression.

Physical and Chemical Constants.

(The Fatty Oil).

Consistency	thin	Sap. value	... 211.0
Sp. gr. at 30°	... 0.9206	Acid value	... 28
Refrac. index at 30°	... 1.4603	Hehner value	... 92.0
Iodine value (Hanus)	... 91.3	Unsaponifiable matter	... 1.6%

Mixed acids.

Mean M.W.	... 294	Sat. acids	... 32.3%
Iodine value (Hanus)	... 93.2	Unsat. acids	... 67.7%

Composition of the Mixed Fatty Acids.

The oil (120 g.) was saponified in the usual manner with alcoholic sodium hydroxide. After distilling off alcohol the resultant soap was dissolved in water and the mixed acids liberated by the addition of strong hydrochloric acid. These were washed with warm water and neutralised with a 10% solution of sodium hydroxide. The soap solution was evaporated, incorporated with washed filter paper pulp and the resulting mass was dried, powdered and extracted with ether in a Soxhlet to remove the unsaponifiable matter. The mixed acids were liberated from the residual soap and purified in the usual manner.

The mixed acids (85 g.), free from the unsaponifiable matter, were separated into solid and liquid acids by Twitchell's lead salt method (*Ind. Eng. Chem.*, 1921, 13, 806) and were found to possess the following constants.

Acids.	Iodine value.	Mean M. W.	Net weight.
(S) Solid	2.55	272.2	27.5 g.
(L) Liquid	65.60	507.5	57.5 g.

The low iodine value and the high mean M. W. were evidently due to polymerisation of the liquid acids as a result of their standing in contact with the laboratory atmosphere for some time.

Solid Acids (S).

The solid acids (27.2 g.) were dissolved in 200 c.c. of methyl alcohol containing 3.5% of dry hydrochloric acid and the solution refluxed for 5 hours. Methyl alcohol was distilled off and the resulting methyl esters were washed with saturated salt solution, water and 5% sodium carbonate and finally with water. After drying under vacuum, 27 g. of the esters were distilled at 6 mm. into the following fractions.

Fractions.	B.p.	Mean M.W. (of the acids)	Net wt.	Component methyl esters			
				Myristate.	Palmitate.	Stearate.	Lignocerate.
S ₁	-172°	247.6	1.0 g.	0.8	0.2	—	—
S ₂	172-75°	269.3	12.5	—	12.5	—	—
S ₃	175-78°	287.0	3.5	—	1.4	2.1	—
S ₄	178-82°	294.0	3.0	—	—	3.0	—
S ₅	182-210°	296.0	6.0	—	—	6.0	—
Residue	—	—	0.8	—	—	—	0.8
Loss	—	—	0.2	—	—	—	—
Total	—	—	27.0	0.8	14.1	11.1	0.8
Per cent.	—	—	100.0	3	52.6	41.4	3

All these fractions were separately saponified and the corresponding acids were liberated and dried in the usual manner.

Acids from fraction S₁ on crystallisation from dilute acetone gave a product melting at 53°. Its mixed melting point with an authentic sample of myristic acid was 52-54°. From the mother-liquor on evaporation and drying a product (mean M. W. 259) was obtained. The fraction, therefore, appeared to be mostly myristic acid accompanied with some palmitic acid.

Acids from fraction S₂ on crystallising twice from dilute acetone gave a product, m.p. 62-63°, M.W. 258. Its mixed melting point with an authentic sample of palmitic acid remained unchanged. The mother-liquor on evaporation and drying yielded a product, M.W. 259. The fraction was thus almost entirely palmitic acid.

Acids from fraction S₃ on crystallising thrice from acetone gave crystals, m.p. 67-68°, M.W. 281. Their mixed melting point with a pure sample of stearic acid remained unchanged. From the mother-liquor a product (M.W. 260) was obtained. It thus appeared that the fraction consisted of palmitic and stearic acids.

Acids from fractions IV and V being similar (mean M.W. 280 and 282) were mixed together and crystallised twice from acetone giving crystals, m.p. 67-68°, M.W. 283. Their mixed melting point with an authentic sample of stearic acid did not show any change. The residue from the mother-liquor had a mean molecular weight of 285.6. The fractions thus entirely consisted of stearic acid.

Acids from the undistilled residual esters after three crystallisations from acetone gave a product, m.p. 75-76°, M.W. 369.2. Its mixed melting point with a sample of pure lignoceric acid showed no change. The acid was, therefore, lignoceric. The mother-liquor being highly coloured and the amount of dissolved acid being small, it was not examined further.

Liquid Acids.

Oxidation.—The liquid acids were saponified to break up any ethyl esters which might have been formed during the Twitchell's separation. A portion of the de-esterified acids was converted into potassium soaps and oxidised in cold alkaline solution with dilute potassium permanganate according to the modified method of Hazura (Lewkowitsch, "Chemical Technology and Analysis of Oils, Fats and Waxes," 6th Ed., Vol. I, p. 575). From the precipitated oxidised acids, dihydroxystearic acid, m.p. 131-32°, M.W. 315, and the tetrahydroxystearic acid, m.p. 155-56°, M.W. 350, were isolated and identified. The filtrate yielded azeleic acid, m.p. 101.2°, M.W. 186, and caproic acid, M.W. 116, indicating that the oxidation of oleic and linoleic acids present in the liquid acids had partly proceeded to rupturing the double bonds between the 9 and 10 carbon atoms in the case of oleic acid and the double bonds between the 9 and 10 and 12-13 carbon atoms in the case of linoleic acid.

Bromination.—Freshly prepared mixed acids (1.6581 g.) were brominated, according to the method of Eibner and Muggenthaler (Lewkowitsch, *loc. cit.*, p. 585) yielding 2.5441 g. of the brominated product (theoretical yield 2.6375 g.) but no hexa- or higher bromides. Crystallised from petroleum ether the brominated product gave white needles (m.p. 113-14°, M.W. 595) which were evidently those of tetrabromostearic acid, m.p. 113-14°, M.W. 600. This was confirmed by the mixed melting point with a sample of pure tetrabromostearic acid from other sources. The oxidation and bromination results thus clearly showed that the liquid acids consisted of only oleic and linoleic acids.

The above data on calculation gave the percentage of the constituent acids as follows:—myristic (1%), palmitic (17%), stearic (13.4%), lignoceric (1%), oleic (31.8%), and linoleic (35.9%).

Unsaponifiable Matter.

The unsaponifiable matter, obtained from the sodium soaps of the mixed acids by extraction with ethyl ether, when crystallised from 95 %

alcohol gave white plates, m.p. $125-26^{\circ}$, which on recrystallisation from the same solvent melted at $131-32^{\circ}$ (acetate, m.p. $124-25^{\circ}$). The mother-liquor on concentration yielded plates, m.p. $125-26^{\circ}$ (acetate, m.p. $124-25^{\circ}$). The unsaponifiable matter thus appeared to contain the common phytosterol, sitosterol, found in many vegetable fats. The residue burnt with a smoky flame and was insoluble in concentrated sulphuric acid and, therefore, appeared to consist mostly of hydrocarbons. The quantity was, however, small for further examination.

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