

Iodine Value (I. V.) Range	Appropriate weight of sample in grams—	
	0.1 N Thiocyanogen Sol.	0.2 N Thiocyanogen Sol.
275-250	0.07-0.08	0.14 -0.155
250-225	0.08-0.09	0.155-0.17
225-200	0.09-0.10	0.17 -0.185
200-175	0.11-0.12	0.185-0.215
175-150	0.12-0.13	0.215-0.24
150-125	0.13-0.14	0.24 -0.26
125-100	0.14-0.15	0.26 -0.28
100-75	0.15-0.16	0.28 -0.30

*Composition of perilla oil:* In the course of isolating and purifying hexabromostearic acid from the brominated mixture of fatty acids of high-iodine number perilla oil\*, the absence of any contaminating tetrabromostearic acid was noticed. A careful examination of the brominated products from a kg. of perilla oil fatty acids failed to give any trace of the characteristic crystalline tetrabromostearic acid. It was tentatively concluded that the amount of linoleic acid present was too small to be detected by bromination.

In further support of this conclusion, the composition of the perilla oil was determined from calculations based on the Wijs I. V., 203.9; T. V., 127.1 (0.1 N, 20°, 24 hrs.); and the (Bertram) saturated acid content, 9.09 percent. The T. V.'s for triolein (85.7), for trilinolein (89.8), and for trilinolenin (154.2) were used in the equations for the calculations. These values were computed from the found thiocyanogen values for the methyl esters reported in Tables I to III. The fatty acid composition, computed to the glycerides, was found to be oleic 17.97, linoleic, 0.00, linolenic, 72.47, and saturated, 9.56 percent.

For comparison, the composition calculated from Kaufmann theory values was found to be: oleic 2.08, linoleic, 32.68, linolenic, 55.68, and saturated, 9.56 percent.

It is apparent from the work of others and from the data in this paper that revision of "Kaufmann theory" values is necessary. It is suggested that since reasonably good agreement was obtained between various workers (Table XI), the average of the found values for oleic,

linoleic and linolenic acids be used in the equations for calculation of composition in place of the Kaufmann-theory values.

### Summary

Thiocyanogen values were determined on the methyl esters of oleic, linoleic and linolenic acids and on six different mixtures of these esters, using 0.1 and 0.2 normal thiocyanogen solutions. The values determined with 0.1 N solutions showed less variation than those determined with 0.2 N.

The composition of the mixtures calculated from equations based on the found thiocyanogen values of the esters agreed with the known composition within reasonable limits. Comparisons were made with the composition calculated with the Kaufmann-theory values.

It is suggested that the F.A.C. consider adopting tentatively the values 89.4 for oleic acid, 93.9 for linoleic acid, and 162.0 for linolenic acid when 0.1 N thiocyanogen solutions are used; the values 89.4, 96.8, and 167.5 when 0.2 N solutions are employed. These represent the average of the values for these acids which have been reported in the literature.

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## An Investigation of Oil from Seed of *Hygrophila Spinosa*\*

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**H**YGROPHILA SPINOSA (Indian name—Tal makhana) of natural-order acanthaceae, is a little annual plant found in abundance throughout India and Ceylon in moist places or on the banks of ponds. Its seeds, which are very small (diameter approximately 1 mm.) in size and deep brown in color, are very light, 100 seeds on an average weighing about 1 gram.

The root, leaves and seeds of this plant find a prominent place in Hindu medicine. The seeds are diuretic and aphrodisiac and are used by Unani physicians in the treatment of gonorrhoea, impotence, spermatorrhoea, and general debility.

In the present communication, a quantitative statement of the component acids of the *hygrophila spinosa* seed oil is given.

Phalnikar et al. (1) have analyzed the oil from the

seeds of *hygrophila spinosa*; the results of their analysis, along with those of the present study, are given in Table I below, from which it will be seen that the present fat differs markedly from the one studied by the above authors.

TABLE I.

	Phalnikar et al. %	Present work %
Myristic acid .....	1.4	1.4
Palmitic acid .....	18.2	5.4
Stearic acid .....	5.4	11.9
Oleic acid .....	75.0*	9.8
Linoleic acid .....		71.5
Unsaponifiables .....	7.5	2.3
(% on oil)		

\*Proportions of oleic and linoleic acids are not given.

The seeds, obtained locally (the United Provinces, India), were freed from dust and other foreign impurities and extracted with petroleum ether (40°-60°C.)

\* From the thesis of P. D. Srivastava, approved for D.Sc. of Benares Hindu University, Benares, India.

in a Soxhlet's apparatus. The oil obtained (23 percent), after removing the solvent, was liquid at room temperature and yellow in color, the characteristic values of which are given in Table II.

TABLE II.

Specific gravity 30°/30° .....	0.9254
Refractive index 30° .....	1.4588
Saponification value .....	196.4
Acid value .....	4.2
Iodine value .....	126.3
Water-insoluble fatty acids .....	94.2%
Unsaponifiable matter .....	2.3%
Iodine value of unsaponifiable matter.....	131.4

Component Acids

The oil (150 g.) was hydrolyzed and the fatty acids (S.E. 278; I.V. 133.7) were then separated into "solid" (17.2 percent) and "liquid" (82.8 percent) acids by means of the differing solubility of their lead salts in alcohol (modified Twitchell's method) (2).

Each group of acids was then converted into the corresponding methyl esters which were fractionally distilled under vacuum from a Willstätter bulb.

The fractionation data are given below in Tables III and IV:

Fractionation Data

TABLE III.

Methyl Esters of "Solid" Acids (S)—S.E. 290.2; I.V. 6.92.			
Fraction No.	Weight Grams	S.E.	I.V.
S <sub>1</sub> .....	2.09	285.0	2.7
S <sub>2</sub> .....	3.61	285.6	3.5
S <sub>3</sub> .....	2.26	287.1	4.1
S <sub>4</sub> .....	2.53	288.5	4.8
S <sub>5</sub> .....	2.63	289.6	7.8
S <sub>6</sub> (residue) .....	4.45	314.4	21.4
	17.57		

TABLE IV.

Methyl Esters of "Liquid" Acids (L)—S.E. 314.1; I.V. 139.5.			
Fraction No.	Weight Grams	S.E.	I.V.
L <sub>1</sub> .....	3.15	286.6	140.1
L <sub>2</sub> .....	1.17	290.1	147.8
L <sub>3</sub> .....	4.50	292.0	162.7
L <sub>4</sub> .....	6.90	194.4	163.4
L <sub>5</sub> .....	3.71	297.0	152.3*
L <sub>6</sub> (residue) .....	9.74	356.8	107.3*
	31.17		

\*Note: This fall in the I. V. is perhaps due to polymerization products; the component acids of these fractions, however, will be the same as those of other fractions.

Examination of Individual Ester Fractions

Fractions S<sub>1</sub>-S<sub>5</sub>: Acids obtained from these fractions, after repeated crystallization from 90 percent alcohol, had almost the same melting point (63°-66°C.), hence, no acid lower than palmitic is present.

Fraction S<sub>6</sub>: The residual fraction S<sub>6</sub> contained acids which, when freed from unsaponifiable matter, had S. E. 283.4 and I. V. 11.5. These acids, after repeated crystallization from 90 percent alcohol, melted at 68°C. and this melting point remained unchanged on mixing with authentically pure stearic acid. Presence of stearic acid is thus confirmed. No acid higher than stearic seems to be present.

Fraction L<sub>6</sub>: The acids from this fraction, after removing the unsaponifiable matter, had S. E. 280.6 and I. V. 96.8.

Fractions L<sub>4</sub>-L<sub>6</sub>: Part of the acids obtained from

these fractions were dissolved in ether and brominated in the usual way. Even after keeping the mixture at 0°C. for about three hours, no precipitate appeared, thus indicating the absence of any linolenic acid. The residue from the above, after removing ether, however, gave, on treatment with petroleum ether (B.P. 40°-60°), at 0°C., insoluble tetrabromide which, after repeated crystallization, melted at 113°C. The presence of ordinary linoleic acid, occurring in the seed fats was thus confirmed.

Another portion of the same acids, in solution in dilute alkali, was oxidized in cold by potassium permanganate solution by the method of Lapworth and Mottram (3).

The products of oxidation were extracted with light petroleum to remove saturated acids. The products insoluble in petroleum were separated into hot water-soluble and insoluble portions. The former yielded, on recrystallization, an acid which melted at 154°-155°C. (no depression in M. P. when mixed with tetrahydroxy stearic acid, M. P. 155°C.); and the latter on treatment with hot ethyl acetate yielded an insoluble acid which on repeated crystallization melted at 170°-171°C. (M. P. remained unchanged when mixed with tetrahydroxy stearic acid, M. P. 171°C.), while from the soluble portion, dihydroxy stearic acid, M. P. 130°C. was isolated.

Thus, among the unsaturated acids, the presence of two types of linoleic acid; one giving a tetrahydroxy stearic acid (M.P. 154°C.); and the other a tetrahydroxy stearic acid (M.P. 171°C.); and delta 9 oleic acid was confirmed. Linolenic acid appears to be totally absent.

From the foregoing qualitative and quantitative data, the composition of the mixed acids present in the oil was calculated as given in Table V:

TABLE V.

Acids	Component Acids.			Fatty Acids Except Unsapon.	
	Solid (17.2%)	Liquid (82.8%)	Total	% Wt.	% Mol.
Myristic .....		1.34	1.34	1.4	1.7
Palmitic .....	4.48	0.69	5.17	5.4	5.9
Stearic .....	11.27		11.27	11.9	11.6
Oleic .....	1.20	8.14	9.34	9.8	9.7
Linoleic .....		67.90	67.90	71.5	71.1
Unsaponifiable .....	0.25	4.73	4.98		

Thus the component fatty acids of hygrophila spinosa seed oil contain about 72 percent of linoleic, 10 percent of oleic, 12 percent of stearic, and 6 percent of palmitic and myristic acids. (Percentage of saturated acids as found by Bertram's method was 18). It can therefore be a good source of linoleic acid.

The oil itself can, however, be classed under semi-drying oils since it contains no linolenic acid. Although the seeds are cheap and plenty, the oil content is rather low to utilize the seeds for any commercial purpose.

It would, however, be interesting to study the drying property of the oil since a very high proportion of linoleic acid with comparatively small proportion of oleic and saturated acids might make it a good vehicle for certain types of varnishes or artistic colors.

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