Chemical Investigation of the Seed-Oil of Leucaena Glauca, Benth.

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LEUCAENA GLAUCA, a tree indigenous to India, belongs to the sub-family Mimosacae of the N. O. Leguminosae. The seeds and leaves are used as a valuable food for cattle (1). A review of the literature indicates that the seed oil of the Formosan variety has been examined by Kinzo Kafuku and his collaborators (2), who reported that the oil contains 29% saturated acids (myristic, palmitic, stearic, behenic), and 71% unsaturated acids (equal amounts of oleic and linoleic acids). As their results do not give a clear account of the percentage of individual acids, the present authors considered it of interest to subject the oil from the Indian variety to a more systematic chemical examination by applying the ester-fractionation method.

The presence of oleic and linoleic acids was established by the bromination and oxidation of the fatty acids derived from the lead-salts soluble in alcohol, but no linolenic could be detected, thus lending support to the view put forward by Grindley (3) that the latter acid is absent in any of the oils belonging to this sub-family so far investigated. Palmitic, stearic, behenic, and lignoceric acids were identified in specific fractions of the hydrolyzed "solid" esters. Attempts to isolate any lower acid other than palmitic failed to disclose the presence of myristic acid, but, on the other hand, lignoceric acid (0.67%) has been found to occur in this oil, not mentioned earlier. Quantitative estimation of the composition of the mixed fatty acids of this oil shows that it differs from that of Formosan variety. Further, it is interesting to note that the major component acids (oleic and linoleic) of this oil are nearly in the proportion of 1:2 whereas this ratio in the case of Mimosacae seed-oils of Sudan varies from 2:1 to 3:4, according to the species (3).

Experimental

The dried and finely powdered seeds on extraction with petroleum ether (b.p. 40-60°C.) gave a dark green oil, bearing the following characteristics:

Fat content	8.8%
Sp. Gr. at 28°C.	0.91648
Ref. Index at 28°C.	1.4674
Sap. value	184.95
I.V. (Hanus)	110.11
Acidity (as % oleic)	2.97
Unsaponifiable	4.7%

The oil on saponification and subsequent hydrolysis, after removal of unsaponifiable matter, yielded 91.5% of free fatty acids. The fatty acids were then resolved into their solid and liquid components by Twitchell's lead-salt-alcohol process and found to be composed of 20.3% solid and 79.7% liquid acids. An estimation of the saturated acids by modified Bertram's method (4) gave 20.8% of saturated acids.

The three groups of fatty acids have the following constants:

	I.V.	S.V.	Calc. Mean Mol. Wt.
Total acids	111.5	200.5	279.8
Liquid fatty acids	135.3	199.9	280.7
Solid fatty acids	6.2	206.2	272.6

TABLE I

Methyl Esters of Liquid Acids

Fr.	Wt./g.	B.P./3 mm.	I.V.	S.E.	Calculated composition Wt./g.			
					Palmitate	Oleate	Linoleate	Unsap.
L_1	10.30	up to 158°C.	124.5	285.3	1.57	2.58	6.15	......
L_2	13.73	158-62°	142.15	291.9	0.51	3.91	9.31	......
L_3	11.71	162-64°	146.65	293.2	0.08	3.44	8.19	......
L_4	12.20	164-68°	146.8	293.8	......	3.61	8.59	......
L_5	10.67	168° falling	139.3	290.9	......	3.16	7.51	......
L_6	11.95	Residue [a]	77.0	333.1	......	3.39	8.08	0.48
Total	70.56				2.16	20.09	47.83	0.48
			% as esters % as acids		3.06 3.05	28.48 28.50	67.78 67.77	0.68 0.68

TABLE II

Methyl Esters of Solid Acids

Fr.	Wt./g.	B.P./4 mm.	I.V.	S.E. (corrected)	Calculated composition Wt./g.				
					Saturated				Unsaturated Oleate
					C_{16}	C_{18}	C_{20}	C_{24}	
S_1	5.87	up to 163°C.	1.68	271.2	5.50	0.27	......	......	0.10
S_2	6.83	163-65°	1.61	274.3	5.58	1.12	......	......	0.13
S_3	7.65	165-67°	2.37	277.3	5.36	2.08	......	......	0.21
S_4	4.92	167-72°	4.00	289.3	1.30	3.39	......	......	0.23
S_5	2.32	172-83°	4.71	308.4	......	1.72	0.47	......	0.13
S_6	7.43	Residue	6.40	358.4	......	......	5.73	1.15	0.55
Total	35.02				17.74	8.58	6.2	1.15	1.35
			% as esters % as acids		50.66 50.43	24.50 24.51	17.7 17.85	3.28 3.32	3.86 3.89

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[a] S.E. of L_6 after removal of unsaponifiable = 305.3. The high S.E. of L_6 even after correction for unsaponifiable indicates the possibility of the presence of small amounts of C_{20} unsaturated acids. We have preferred however to leave this open and include all in oleic and linoleic on the basis of the I.V. of the previous fraction (L_5).

The liquid and solid fatty acids were separately converted into methyl esters and systematically fractionated under vacuum. The percentages of the individual saturated acids in each ester fraction have been calculated according to the method of Baughman and Jamieson (5). The amounts of palmitic and C_{18} mono- and di-ethenoid acids and unsaponifiable in liquid esters are estimated on the basis of iodine values and saponification equivalents in conjunction with qualitative examination of each ester fraction. The results of the ester-fractionation are tabulated below.

Identification of Fatty Acids

Unsaturated acids. The oleic and linoleic acids were identified in the "liquid" ester fractions (L_1-L_5) in the form of their oxidation products (9:10 dihydroxy-stearic acid, m.p. 130°C.; 9:10:12:13 tetrahydroxy-stearic acid, m.p. 174°C.) obtained by the permanganate oxidation of the regenerated acids. Traces of palmitic acid (m.p. 59-61°) were isolated in the lowest boiling fractions (L_1-L_3) of liquid acid esters from light petroleum ether extracts of the oxidized product, followed by crystallization from aqueous alcohol. Further evidence of the presence of linoleic acid was obtained by the isolation of a tetrabromide m.p. 113-14° (which showed no depression on admixture with an authentic sample). No ether-insoluble hexabromide could be isolated, thus confirming the absence of linolenic acid in the liquid acids.

Saturated acids. The acids from each ester fraction were isolated and identified by their melting and mixed melting points.

Fractions

S_1-S_4: Palmitic acid, m.p. 59-61°; stearic acid, m.p. 69-71°.
S_5: Stearic acid, m.p. 68-70°; behenic acid, m.p. 78-80°.
S_6: Behenic acid, m.p. 78-80°, mean. mol. wt., 344.5 lignoceric acid, m.p. 78-80°, mean. mol. wt., 366.2.

The S.E. of the residue (S_6), which is in between that of methyl-behenate and methyl-lignocerate, clearly indicates their presence in this fraction.

TABLE III
Calculated Composition of Total Fatty Acids

	Solid	Liquid	Total	Excluding unsaponifiable
	%	%	%	%
	20.3	79.7	100.0	
Saturated acids				
Palmitic	10.24	2.43	12.67	12.74
Stearic	4.98	......	4.98	5.01
Behenic	3.62	......	3.62	3.64
Lignoceric	0.67	......	0.67	0.67
Unsaturated acids				
Oleic	0.79	22.71	23.50	23.63
Linoleic	......	54.01	54.01	54.31
Unsaponifiable	......	0.55	0.55	....

Examination of the Unsaponifiable Matter

The unsaponifiable matter obtained, prior to the liberation of the mixed fatty acids, when crystallized from absolute alcohol gave white crystalline needles m.p. 139-40°C. This appears to be sitosterol.

Summary

The fixed oil from the seeds of *Leucaena glauca*, Benth. (N. O. Leguminosae) has been studied for its component acids. The fatty acid composition, as determined by the ester-fractionation analysis, was found to be palmitic (12.74%), stearic (5.01%), behenic (3.64%), lignoceric (0.67%), oleic (23.63%), and linoleic (54.31%). The latter unsaturated acids are the major components.

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Metal Inactivation in Edible Oils by Carboxymethylmercapto Succinic Acid[1]

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INVESTIGATIONS with model compounds and the formulation of a theory to explain their activity in stabilizing soybean oil has led to the investigation of a new stabilizer possessing high activity. It is carboxymethylmercapto succinic acid and is relatively new to the chemical field.

Carboxymethylmercapto succinic acid, $HOOCCH_2$-$SCH(COOH)CH_2COOH$, has two carboxyl groups, alpha to the sulfur atom and one carboxyl group in the beta position. This arrangement of functional groups is ideal for the formation of chelate rings and the complexing of iron in an octahedral configuration (6, 7). Actually the molecule has one more carboxyl group than is necessary for complexing the iron, and it has been shown that this carboxyl group can be successfully esterified to achieve oil solubility and that the compound will still retain excellent metal-scavengering properties (15).

The preparation of carboxymethylmercapto succinic acid is described by Morgan and Friedmann (9) and by Larsson (4). This acid has recently been made available from production on a pilot-plant scale.[3] Es-

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