CHEMICAL EXAMINATION OF THE FRUITS OF *TERMINALIA BELERICA* ROXB.

Part II. The Component Clycerides of the Fatty Oil

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[The component glycerides of the seed oil of *Terminalia belerica* have been examined. The amounts of oleic, linoleic, palmitic and stearic acids have been found to be in fair agreement with those reported[1] in Part I. The component glycerides of the oil are Palmitooleolinolein 35·24%, Stearooleolinolein 43·51%, Palmitodiolein 1·07%, Stearodiolein 1·95%, Dioleolinolein 9·54% and Triolein 8·69%.]

In a previous communication,[1] the percentage composition of the component fatty acids of the oil from the kernels of the fruit of *Terminalia belerica* (natural order *Combretaceæ*) has been reported by Saran and Singh; the present work is in continuation of it and deals with the glyceride structure of the oil. A few other species of *Terminalia* have also been examined for the composition of seed oil, namely, *T. catappa* from East Indies[2] and West Africa[3] and *T. chebula*.[4] The major component acids of these oils are oleic, linoleic and palmitic, stearic acid being present in only minor proportions. The fatty acid composition of *T. belerica* as found directly by Saran and Singh is in fair agreement with that determined from the glyceride composition of the oil as shown below:

	Oleic	Linoleic	Palmitic	Stearic
Saran and Singh (direct determination) ..	43·21%	28·99%	11·80%	16·00%
Present authors (glyceride structure) ..	43·68%	29·56%	11·28%	15·48%

It will be thus seen that oleic and linoleic acids are the major components of all *Terminalia* species, the amount ranging between 56 to 84%. There is, however, this difference that whereas stearic acid is present only in minor proportions and is not a major component in other species of *Terminalia* so far investigated, it becomes a major component (over 15%) along with palmitic acid (over 11%) in the seed oil of *T. belerica*.

The number of glycerides present in the seed oil of *T. belerica* is found to be six, whereas the total number of glycerides which can be formed from four acids and the glyceryl radical, $CH_2-CH-CH_2$, is forty.

EXPERIMENTAL

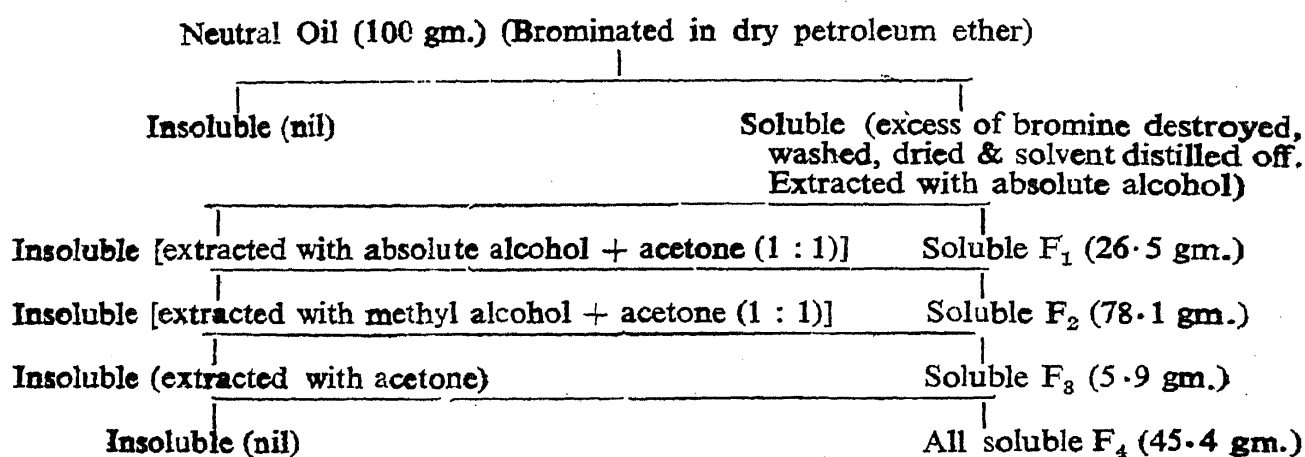The oil extracted from the crushed kernels of the fruit of *T. belerica* with petroleum ether (40°–60°) was purified with animal charcoal and Fuller's earth, dried over fused calcium chloride, neutralised with sodium carbonate and filtered.

One hundred grams of the oil was chilled[5,6] in the frigidaire with six times its weight of pure and dry acetone for a week. No solid separated showing the absence of trisaturated and disaturated-monounsaturated glycerides. The experiment was repeated twice with each of the following samples of the oil:—

(*a*) Freshly extracted and purified oil, (*b*) about one year old oil, and (*c*) sample of oil used by Saran and Singh, but in no case any solid glyceride separated. The absence of trisaturated glyceride was further confirmed by oxidising the oil dissolved in pure and dry acetone with powdered potassium permanganate.[7]

One hundred grams of the oil was brominated[8,9] in ten times its weight of dry petroleum ether (40°–60°) at − 5° C. till the brown colour persisted. It was kept in the frigidaire overnight. No solid separated. Excess of bromine was destroyed with sodium thiosulphate solution, washed, dried over fused calcium chloride and the solvent distilled off. The viscous residue was extracted with absolute alcohol, absolute alcohol + acetone (1 : 1), methyl alcohol + acetone (1 : 1) and acetone in succession.

The scheme of separation is given below:—

Neutral Oil (100 gm.) (Brominated in dry petroleum ether)

Insoluble (nil)　　　　　Soluble (excess of bromine destroyed, washed, dried & solvent distilled off. Extracted with absolute alcohol)

Insoluble [extracted with absolute alcohol + acetone (1 : 1)]　　Soluble F_1 (26·5 gm.)

Insoluble [extracted with methyl alcohol + acetone (1 : 1)]　　Soluble F_2 (78·1 gm.)

Insoluble (extracted with acetone)　　Soluble F_3 (5·9 gm.)

Insoluble (nil)　　　　　All soluble F_4 (45·4 gm.)

The fractions F_1, F_2, F_3 and F_4 were debrominated by taking them in methyl alcohol, adding zinc dust, saturating with dry hydrogen chloride gas

and heating for several hours under reflux in the water-bath. The brominated products were saponified, the unsaponifiable matter removed and the mixed fatty acids liberated. The quantity of individual acids in each fraction was estimated by determining their saponification equivalent and iodine and thiocyanogen values. The quantities of saturated acids being too small in these fractions for estimating them separately, they were considered as one acid and their mean molecular weight determined on extracting with petroleum ether (40°–60°), the oxidation products of each fraction with alkaline potassium permanganate.[10] The glyceride structure was calculated with these data as given below in Tables I to VI.

TABLE I

	F_1	F_2	F_3	F_4
Weight of Brominated glyceride in grams ..	26·5	78·1	5·9	45·4
,, Unsaponifiable matter in gm. ..	·25	·26	·002	·011
,, Debrominated glyceride in gm. ..	17·52	49·82	3·72	28·95
,, ,, ,, free from un-saponifiable matter	17·27	49·56	3·72	28·94
Weight % of acid ..	17·36	49·80	3·74	29·10
Mol. % of acids ..	17·24	50·13	3·73	28·90
Iodine value of liberated acids ..	84·98	93·09	97·45	96·58
Thiocyanogen value of liberated acids ..	59·94	64·03	67·84	73·00
Mean molecular weight of ,, ,, ..	276·5	272·7	275·1	276·7
Mean molecular weight of solid acids ..	275·0	270·4	273·9	275·4

TABLE II. *Weight % of acids in different fractions*

	F_1	F_2	F_3	F_4
Linoleic ..	27·64	32·07	32·68	26·03
Oleic ..	38·81	38·89	42·51	54·95
Solid ..	33·55	29·04	24·81	19·02

TABLE III. *Weight % of acids on total acids*

	F_1	F_2	F_3	F_4	Mean
	17·36	49·80	3·74	29·10	100
Linoleic ..	4·80	15·96	1·22	7·58	29·56
Oleic ..	6·74	19·36	1·59	15·99	43·68
Solid ..	5·82	14·48	0·93	5·53	26·76

TABLE IV.   *Mol. % of acids in different fractions*

	F_1	F_2	F_3	F_4
Linoleic ..	27·53	31·81	32·58	26·04
Oleic ..	38·39	38·32	42·09	54·64
Solid ..	34·08	29·87	25·33	19·36

TABLE V.   *Mol. % of acids on total acids*

	F_1	F_2	F_3	F_4	Mean
	17·24	50·13	3·73	28·90	100
Linoleic ..	4·74	15·95	1·21	7·53	29·43
Oleic ..	6·62	19·21	1·57	15·78	43·18
Solid ..	5·88	14·97	0·95	5·59	27·39

TABLE VI.   *Probable glyceride structure*

	F_1	F_2	F_3	F_4	Mean
	17·24	50·13	3·73	28·90	100
1 Trisaturated glyceride ..	Nil	Nil	Nil	Nil	
2 Disaturated monounsaturated ..	,,	,,	,,	,,	
3 Monosaturated diunsaturated—					
(a) , oleolinolein ..	14·22	44·91	2·85	16·77	78·75
(b) ,, diolein ..	3·02	3·02	..	..	3·02
Triunsaturated—					
(a) Dioleolinolein ..	..	2·94	0·78	5·82	9·54
(b) Triolein ..	..	2·28	0·10	6·31	8·69

1. By oxidizing the neutral oil dissolved in pure and dry acetone with powdered potassium permanganate.

2. By chilling the neutral oil dissolved in pure and dry acetone at 0° C.

3 & 4. By calculating from the component fatty acids of the brominated glyceride in the oil.

All the saturated acids have been considered as one acid in the calculation of monosaturated-diunsaturated glycerides. According to the law of even distribution we are justified in assuming that the greater proportion of glycerides exist as monosaturated oleolinolein rather than monosaturated diolein and monosaturated-dilinolein. Further it has been assumed that the solid acids are proportionally divided in different glycerides. From the

above considerations the probable glyceride structure may be given as: Palmitooleolinolein 35·24%, Stearooleolinolein 43·51%; Palmitodiolein 1·07, Stearodiolein 1·95%, Dioleolinolein 9·54% and Triolein 8·69%.

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