THE GLYCERIDE COMPOSITION OF FATS AND OILS

Part II. The Fatty Acids and Glycerides of *Terminalia belerica* (Roxb.)

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OILS of *Terminalia* genus have been little investigated. Of the three more important species *Terminalia catappa*[1, 2] (Indian almond), *Terminalia chebula*[3] and *Terminalia belerica*,[4] only the first has been examined by the ester fractionation method; the oil from *Terminalia chebula* has merely been separated into saturated and unsaturated acids while *Terminalia belerica* oil does not seem to have been investigated in detail at all. No member of this genus has been investigated with regard to the glyceride structure till now.

The first examination of oil of *Terminalia belerica* seems to have been made by Hefter[5] who, however, has reported only that the seed kernel yields 44% of a fatty oil which consists of solid and liquid glycerides. Hooper[6] has recorded some constants of two specimens of the oil. We have now examined two specimens of the oil for component acids, one by ester fractionation procedure and the other by the simple but equally accurate Bertram procedure. The component acids consist of palmitic and stearic with a little arachidic in the saturated series and probably only oleic and linoleic acids in the unsaturated class. All the three species of *Terminalia* are characterised by the presence of about 25% of linoleic acid (see below). *Terminalia catappa* and *Terminalia belerica* show a closer resemblance in

	Weight percentage on total acids					
	Saturated				Unsaturated	
	C·14	C·16	C·18	C·20	Oleic	Linoleic
T. catappa—1 ..	1·0	29·0	4·1	0·8	41·7	23·4
2 ..	..	34·0	9·7	0·4	27·3	28·6
T. chebula ..	..	17·8	..	..	58·8	23·4
T belerica :						
Ester method ..	..	22·4	15·7	0·8	28·1	33·0
Bertram method ..	..	20·5	20·8	..	26·7	32·0

the large amount of saturated acids which they contain, though those of the latter consist principally of palmitic acid while those of the latter consist of about an equal mixture of palmitic and stearic.

We have completed the examination of one specimen of *T. belerica* oil (I.V. 78·5; Saturated acids 41·3%) for the constituent glycerides according to the oxidative method evolved in our laboratory.[8, 10] The absence of fully saturated glycerides in any quantity was proved by a preliminary oxidation which gave only 0·0018 gram of neutral material from 6 grams of the oil. The mean molecular weight of the saturated acids was found to be 270·0 and 270·2 in two separate determinations, their percentages being 39·49 and 39·5 on the weight of the oil. Since fully saturated components were absent, washing of the ethereal solution of the acidic oxidation products leaves behind monoazelao-disaturated glycerides and diazelao-monosaturated glycerides together with any unoxidised fat. The results of two typical examinations are detailed in the experimental section.

As shown in the experimental part, the percentage composition by weight of the component acids of the above specimen of *Terminalia belerica* oil is palmitic 20·50, stearic 20·80, oleic 26·70 and linoleic 32·0; which, as expressed by molecules, is palmitic 22·2, stearic 20·2, oleic 26·1 and linoleic 31·5; thus making a total of 42·4 molecules of saturated acids and 57·6 molecules of unsaturated acids. Of this, 18·6 molecules of saturated acids are combined as GS_2U and none as GS_3, hence the remaining 23·8 molecules are combined as GSU_2, thus forming 71·4 molecules of di-oleo-monosaturated glycerides and the final composition of the oil is: GS_3 traces, GS_2U 28%, GSU_2 71·4% and GU_3 0·6%. The glyceride composition as calculated by some methods of partitioning of the fatty acids among themselves[7] are shown in the accompanying table:

	GS_3	GS_2U	GSU_2	GU_3
Determined ..	Trace	28·0	71·4	0·6
Even distribution ..	0	27·3	71·7	0
Oleic among others ..	12·4	45·0	..	42·6
Linoleic among others ..	3·2	58·8	..	38·0
Oleic among others, then excess of linoleic over oleo dilinolene among saturated	..	59·9	7·4	32·7

The most striking aspect about the glyceride constitution of oil of *Terminalia belerica* is its close approximation to the rule of even distribution which is not met with in many of the other seed fats which we have examined so far. It would, at this point, be of interest to compare the glyceride

composition of a Mowra oil, which we have recently investigated[8] and which had practically the same saturated-unsaturated acid ratio. The component acids are the same and there is not much difference in their proportions except in the relative proportions of oleic and linoleic acids. But the glyceride structure is entirely different in the two cases. This shows that probably the general mode of construction or assembling of the acids into triglycerides need not be the same even in any two vegetable seed fats (compare Hilditch[9]).

Experimental

Weight of oil oxidised	..	5·3788 grams
Weight of azelao glyceride mixture after washing with bicarbonate	..	3·1475 ,,
Saponification value of the mixture	..	359·1
Weight of recovered total saturated fatty acids	..	2·1450 ,,
Iodine value of recovered saturated acids	..	0·90

The iodine value 0·9 of the acids recovered corresponds to the unoxidised portion of the oil. After Bertram separation, the weight of acids is 2·145 grams, which works up to, on the weight of oil, 2·145 × 100/5·3788 or 39·87%. The percentage of unsaturated unoxidised acid will be 0·9 × 39·87/90 or 0·398 on the weight of oil (90 being the iodine value of oleic acid). Since, for purposes of computation, the percentage of unsaturated glycerides (unoxidised) will be approximately thrice the unsaturated acids, the percentage of unoxidised unsaturated glycerides is 0·398 × 3 or 1·2.

A more detailed calculation is as follows :—

282 of oleic acid should give [282 + (2 × 270) + 38] of GS_2U by weight when S is 270 (mean molecular weight in the present instance[2]) or 860. Here the assumption is that of the two mixed unsaturated glycerides (GS_2U and GSU_2) the GS_2U has greater probability of escaping complete oxidation.

The weight per cent. of GS_2U will be 0·398 × 860/282 or 1·205 per cent. 1·2 per cent. of the oil is contained in 3·1475 grams of the azelao glyceride mixture obtained experimentally. Hence the percentage content of unoxidised oil based on the azelao-glycerides mixture will be

$$1·2 \times 5·3788/3·1475 \text{ or } 2·05.$$

The saponification value of 2·05% will be 56·11 × 100 × 3/860 or 195·7. Hence the S. V. of the mono-, and diazelao-glyceride mixture can be calculated. The actual experimental saponification value of the mixture containing GS_3, GS_2U, GS_2A and GSA_2 is 359·1. In this case of course, GS_3 is nil and hence we have now to correct for the saponification value of GS_2U.

If X is the saponification value of the mixture, GS_2A and GSA_2, then $359{\cdot}1 \times 100 = 195{\cdot}7 \times 2{\cdot}05 + (X \times 97{\cdot}95)$, where 97·95 is the sum total of the percentage of GS_2A and GSA_2. Hence X is 362·3.

Weight of mixture of azelao-glycerides is $3{\cdot}1475 \times 97{\cdot}95/100$. The percentage weight of mono-azelao-glycerides is

$$\frac{3{\cdot}1475 \times 97{\cdot}95 \times (410{\cdot}2 - 362{\cdot}3)}{100 \times 5{\cdot}3788\,(410{\cdot}2 - 293)} \times 100 \text{ or } 23{\cdot}42,$$

since saponification value of GS_2A is 293·0 and of GSA_2 is 410·2 (experimental determination gave 410·8) and percentage of GSU_2 by weight is $23{\cdot}4 \times 860{\cdot}2/766{\cdot}2$, 1·2 or 27·5.

In a duplicate experiment 4·4739 grams of oil were oxidised and 2·6020 grams of azelao-glyceride mixture was obtained after washing with bicarbonate. The mixture of glycerides had a saponification value of 358·4. After Bertram separation, the saturated acids obtained weighed 1·7778 grams. The recovered saturated acids had an iodine value of 0·6. Hence percentage of unoxidised fat as oleo disaturated glycerides is 0·8, and percentage of unoxidised fat in azelao-glyceride mixture is 1·4. The percentage weight of azelao-glycerides is $58{\cdot}16 \times 98{\cdot}6/100$. True saponification value of azelao-glycerides is 360·6. Hence percentage weight of monoazelao-glycerides is

$58{\cdot}16 \times 86{\cdot}6/100 \times 49{\cdot}6/117{\cdot}2$ or 24·27.

Percentage of GS_2U by weight is $24{\cdot}27 \times 860{\cdot}2/766{\cdot}2$, 0·8 or 28·0.

Percentage of GS_2U in oil by weight is 27·5, 28·0/2, or 27·75.

Percentage of GS_2U in oil by molecules is 28·0.

Analysis of the Oil by Ester Fractionation—1941 *Sample.*—187 grams of the seed kernel was exhausted with benzene yielding 74·4 grams of the oil corresponding to an yield of 39·8%. 218 grams of the oil was hydrolysed yielding 203 grams of mixed acids of mean molecular weight 277·8; iodine value 87·36; Titre 35; Refractive index (40) 1·4524.

The mixed acids separated into solid and liquid acids by lead salt separation yielded, approximately, 75·2 grams of solid acids and 127·8 grams of liquid acids. They gave the following analytical constants:—

	Solid Acids	Liquid Acids
Refractive Index ..	1·4434 (60)	1·4588
Mean Molecular weight ..	272·6	281·2
Iodine Value ..	1·8	129·4

100 grams of the solid and liquid acids were separately esterified and fractionated. The solid acids fraction consisted of C_{16}—19·93; C_{18}—15·76; C_{20}—0·79; oleic—0·20; linoleic—0·32. The liquid acids fraction consisted of C_{16}—2·45; oleic—27·90 and linoleic—32·64. Hence the components are C_{16}—22·38; C_{18}—15·76; C_{20}—0·79; oleic 28·10 and linoleic 32·96 per cent.

Distillation of Solid and Liquid Acid Esters

No.	Weight	Temperature	S. Equivalent	Refractive Index	Iodine Value
			(*a*) Solid acids		
1	31·48	190–195	293·80	1·4390	0·35
2	29·15	190–195	294·50	1·4390	0·44
3	12·45	195–205	302·20	1·4410	3·85
4	6·27	Residue	318·50	1·4625	14·50
			(*b*) Liquid acids		
1	39·04	200–205	306·4	1·4505	119·7
2	32·23	205–210	309·2	1·4507	123·7
3	20·25	210–215	308·8	1·4510	125·2
4	11·34	Residue	..	1·4624	118·2

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