GLYCERIDE COMPOSITION OF TOBACCO SEED OIL

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The glyceride structure of tobacco seed oil has been determined by brominating the neutral oil followed by isolation of the various individual bromoglycerides by extraction with suitable solvents and estimating the fatty acid composition of these fractions The component glycerides of the oil have been found to be trilinolin (7%), oleodilinolin (35%), dioleolinolin (7%), myristodilinolin (2%), palmitodilinolin (9%), stearodilinolin (6%), myristoleolinolin (5%), palmitoleolinolin (18%), stearoleolinolin (11%). The fat conforms to the usual evenly distributed type in the structure of its component glycerides.

The glyceride structure of natural fats has been widely examined by Hilditch and his collaborators. The methods employed by them (*J. Soc. Chem. Ind.*, 1938, **57**, 44T) in the case of fats containing a high proportion of fully saturated glycerides can not be adopted for a majority of liquid fats, both animal and vegetable, containing a high percentage of triunsaturated acids. The other method of hydrogenating a fatty oil and finding the proportion of the glycerides made up wholly of stearic, oleic, linolic or linolenic acids by fractional crystallisation adopted by Hilditch and Jones (*J. Soc. Chem. Ind.*, 1934, **53**, 13T) in the case of oils containing unsaturated acids belonging to the C_{18} series such as olive, cotton seed, linseed and others of the 'non-drying', and 'drying types', does not throw any light on the association of the different unsaturated acid in the glycerides and is not found useful in the case of fish oils containing unsalurated C_{14} and C_{16} acids.

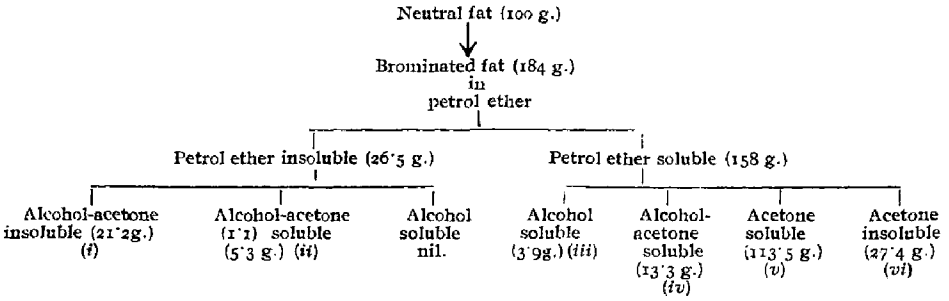
Based on the findings of Susuki and Yokoyama (*Proc. Imp. Acad. Tokyo.*, 1927, **3**, 526, 529; 1929, **5**, 265) Susuki and Masuda (*Proc. Imp. Acad. Tokyo*, 1927, **3**, 551; 1928, **4**, 165; 1929, **5**, 268) and Hashi (*J. Soc. Chem. Ind. Japan*, 1927, **30**, 849, 856; 1928, **31**, 117), Vidyarthi and Mallya (*J. Indian Chem. Soc.*, 1940, **17**, 87) evolved a quantitative method by brominating the neutral oil and separating the solid and liquid bromoglycerides into a mumber of similar fractions by extraction with suitable solvents. This method was used in adducing the glyceride structure of niger seed and safflower oil (*J. Indian Chem. Soc.*, 1940, **17**, 87; 1943, **20**, 45) and it was found useful in determining the component glycerides of tobacco seed oil which like niger seed and safflower oils contains palmitic, oleic and linolic acids as the major component acids and the results for tobacco seed oil have been recorded in this paper.

Experimental

Saturated Glycerides.—100 G. of tobacco seed oil, rendered neutral by treatment with sodium carbonate and filtered through decolourising carbon, were dissolved in 1000 c.c. of dry acetone and left overnight. No precipitate was obtained indicating the absence of trisaturated and disaturated glycerides in the fatty oil. This on oxidation with potassium permanganate gave a very small precipitate which was found to be mainly non-saponifiable matter.

Bromination of the Oil.—100 G. of the neutralised oil were dissolved in a litre of petroleum ether and cooled down to $-5°$. Liquid bromine was slowly added to it drop by drop maintaining the temperature at -5 to $+1°$ till the whole solution acquired a permanent brown colour. The flask together with its contents was left in ice-chest overnight when a crystalline solid was precipitated. The solid bromoglyceride was separated from the mother-liquor and further washed with chilled petroleum ether. The mother-liquor together with the washings was freed from excess of bromine by washing with dilute sodium thiosulphate solution. It was distilled and dried till free from petroleum ether. This residue obtained from the mother-liquor and the solid bromoglyceride were successively extracted with alcohol, alcohol-acetone (1:1) mixture and acetone to separate the bromoglycerides into simpler fractions as indicated in Table I.

TABLE I



Debromination of the Fractions.—Each of the fractions shown in the above table was debrominated by boiling with zinc dust in a solution of methyl alcohol saturated with hydrogen chloride for nearly 2 to 3 hours, zinc dust being added in small quantities at a time till a slight excess was present. The debrominated fraction was extracted with ether and washed free of all mineral acid. It was then saponified and the mixed acids were recovered by decomposing with dilute sulphuric acid after extracting the non-saponifiable matter.

Identification of the Acids.—The individual unsaturated acids were identified by oxidising them with alkaline potassium permanganate. The saturated acids were extracted with petroleum ether from the oxidation products of these fractions and the mean molecular weights of these acids in each fraction determined. As the saturated acids from each fraction were too small in quantity to enable the separation of the individual acids, all the saturated acids of a particular fraction were considered as one acid and the saponification equivalents of these acids were used in finding the mole proportions. The quantity of the individual unsaturated fatty acid in each fraction was estimated by determining the saponification equivalents, iodine values and thiocyanogen values. The analytical results are given in Table II.

TABLE II

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	Total
Wt. of bromoglycerides (g.)	21·2	5·3	3·9	13·3	113·5	27·4	184·6
Sap equivalent of acids	280·2	280·2	276·5	281·1	276·1	280·8	
I. value of acids	168·5	162·9	93·4	141·1	114·3	138·8	
Thiocyanogen value of acids	90·5	90·4	60·4	90·3	68·8	90·3	
Sap. equiv. of saturated acids	—	—	268·0	—	262·6	—	
Wt. of debrominated glyceride free from non-saponifiable matter	10·2	2·45	2·35	7·05	65·5	14·5	
Glycerides on percentage basis	10·0	2·4	2·3	6·9	64·2	14·2	
Glycerides (Mol. %)	9·9	2·37	2·3	6·8	64·6	14·0	

From the above data and the identification of individual unsaturated acids in each fraction the percentage compositions of these acids were calculated (Table III.)

TABLE III

Percentage composition of acids by weight

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	
Oleic acid	12·8	19.0	30·8	43·2	25·2	45·8	
Linolic	87·2	81·0	36·7	56·8	50·9	54·2	
Saturated acids	—	—	33·0	—	23·9	—	
Composition of acids by weight on 100 total acids							
							Total
Oleic	1·3	0·45	0·7	3·0	16·2	6·5	28·15
Linolic	8·7	1·95	0·85	3·9	32 7	7·7	55·8
Sat. acids	—	—	0·75	—	15·3	—	16·05
							100·0
Mol. percent of the acids in the fractions on total acids.							
Oleic	1·28	0·44	0·7	2·95	15·95	6·4	27·72
Linolic	8·63	1·93	0·85	3·87	32·45	7·63	55·36
Sat. acids	—	—	0·78	—	16·17	—	16·95
							100·03

The fatty acid composition, obtained by the bromoglyceride method, agrees within experimental limits with the component fatty acids obtained by the ester fractionation method (*J. Indian Chem. Soc.*, 1943, **20**, 374).

From the above figures the component glycerides of the tobacco seed oil have been calculated and given in Table IV.

TABLE IV

	(i)	(ii)	(iii)	(iv)	(v)	(vi)	Total
Glycerides in fractions (M %)	9·91	2·37	2·31	6·82	64·57	14·02	100·0
1. Fully sat. glyceride	nil	nil	nil	nil	nil	nil	nil
2. Disaturated glyceride	—	—	—	—	—	—	—
3. Monosaturated glyceride							
(*a*) Monosat. dilinolin	nil	nil	0·24	—	16·72	—	16·96
(*b*) Monosat. oleolinolin	nil	nil	2·07	—	31·8	—	33·87
4. Triunsaturated glyceride							
(*a*) Dioleolinolin	—	—	—	2·02	—	5·17	7·19
(*b*) Oleodilinolin	3·84	1 32	—	4·80	16·05	8·86	34·87
(*c*) Trilinolin	6·07	1·05	—	—	—	—	7·12
	9·91	2·37	2·31	6·82	64·57	14·03	

1. By the oxidation of the neutral oil with potassium permanganate in acetone.
2. By the crystallisation of the neutral oil from acetone at 0°.
3. & 4. From the component fatty acids of the brominated fractions.

All the saturated acids have been considered as one acid in the calculation of glycerides. As all the saturated acids are combined with the unsaturated acids in the form of monosaturated glycerides due to the absence of trisaturated and disaturated glycerides, the assumption that these acids are distributed proportionately in mononsaturated dilinolin and monosaturated oleolinoln will not be incorrect. From the molecular percentage of the saturated acids in the oil the component glycerides of tobacco seed oil may be given in round figures as myristoleolinolin (5%) myristodilinolin (2%), palmitoleolinolin (18%), palmitodilinolin (9%), stearoleolinolin (11%), stearodilinolin (6%), dioleolinolin (7%), oleodilinolin (35%), and trilinolin (7%).

The above glyceride structure clearly shows that tobacco seed oil adds to the list of seed fats conforming to the principle of even distribution of the fatty acids in the glyceride molecule. This oil characterised as a semi-drying oil has been found to dry best when boiled with cobalt driers and the drying property comparable to that of niger seed oil. A comprehensive study of the drying properties of the oil is in progrese.

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