THE COMPONENT GLYCERIDES OF VEGETABLE FATTY OILS. PART II. SAFFLOWER OIL

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The safflower seeds (*Carthamus tinctorious*) yield 30·5% of oil which contains myristic acid (along with lauric and other lower acids) 1·5%, palmitic acid (3%), stearic acid (1%), archidic acid with a trace of lignoceric acid (0·5%), oleic acid (33%), linolic acid with a trace of linolenic acid (61%).

The glycerides have been determined by the bromination of the neutral oil and the component glycerides have been found to be myristo-oleolinolin (2%), myristodilinolin (1%), palmito-oleolinolin (7%), palmitodilinolin (4%), stearo-oleolinolin (2%), stearo dilinolin (1%), dioleolinolin (15%), oleo dilinolin (63%) and trilinolin (3%). The myristo glycerides contain a little of lauric and other lower acids, stearo glycerides contain little of archidic and lignoceric acid and the trilinolin contains traces of linolenic acid.

Carthamus tinctorius, Linn., commonly known as safflower (N.O. Compositæ) or Bastard saffron, is cultivated all over India both for oil seed as well as for the dye which is obtained from the flower. There was a time when safflower was considered to be an exceedingly important crop, but with the advent of the aniline dyes the area under cultivation of this crop has shrunk considerably during recent years. The seeds yield about 30% of oil, light pale in colour, which has been found to possess a very good drying property and is considered to be suitable for use in the manufacture of paints, varnish, linoleum etc. [Rabak, *Oil Paint & Drug Reptr.*, 1927, III, No. 583]. A valuable property of this oil is its ability to prevent "after-yellowing" of white or pale tinted paints.

A good deal of work has been done in America and Germany on the composition of the fatty acids of safflower oils of these countries but the only work on the Indian safflower oils appears to have been done by Howard and Remington (*Bull. Agric. Res. Inst. Pusa*, 1921, No. 124, 14), who examined the physical and chemical characteristics of 24 samples of seeds. No work has been done as yet on the composition of the glycerides present in this oil. In general, the composition of fats and fatty oils varies according to the environment under which the seeds are grown. Ivanov, who has studied the effect of climate upon the composition of vegetable fats for a considerable period of years, with particular reference to the drying oils, has formulated (*Chem. Umchau*, 1929, 36, 40) that the climate of southern lands favours the formation of oleic acid, whereas that of northern lands favours the formation of linoleic acids. The investigations have indicated that the flax seed and soyabeans, grown in temperate climates, have higher iodine values than those grown in the tropics. On the basis of this finding the composition of the safflower oil, grown in India, must have a different composition than those grown in America, Germany, Spain and other temperate climates. The present work was taken up with a view to finding out the composition of the fatty acids and the component glycerides of Indian safflower oil as no previous work has been recorded in literature. The methods adopted are similar as those for the determination of the component glycerides of Niger seed oil by Vidyarthi and Mallya (*J. Indian Chem. Soc.*, 1940, 17, 87).

The oil has been found to consist of myristic, lauric and other lower acids 1·5%, palmitic acid 3·0%, stearic acid 1%, archidic and lignoceric acid 5%, oleic acid 35% and linoleic acid 61% and linolenic acido ·1% and the component glycerides have been found to be oleo-myristolinolin 3%, palmito-oleolinolin 7%, oleo-stearolinolin 2%, myristodilinolin 1·0% palmitodilinolin 4%, stearodilinolin 1%, dioleolinolin 15%, oleodilinolin 64% and trilinolin 3%.

The composition of safflower seems to be like that of the niger seeds which belong to the same botanical order. Safflower oil contains higher percentage of linoleic acid and lower of saturated and oleic acids and therefore according to the rules of even distribution dilinoleo glycerides are more than those found in the niger eed oil. Although there is no linolenic acid, the higher percentage of fully unsaturated glycerides accounts for the quick drying property of this oil.

EXPERIMENTAL

The seeds were crushed and the husks were removed as far as possible. The husked seeds were extracted with carbon tetrachloride. The seeds contained 30·5% of oil having the following physical and chemical characteristics.

TABLE I.

Sp. gravity at 27°	0·9242	Acid value	6·3
Refractive index at 27°	1·4742	Non saponifiables	1·3
Saponification value	192·0	Acetyl value	13·2
Iodine value (Wijjs)	136·2	Hexa bromide value	0·2%.

450 G. of the oil were saponified. The soap was mixed with sand and dried till it was friable, after which it was extracted with acetone. The solvent was distilled off from the extract and the residue was taken up in water and extracted with ether. The ethereal solution was washed free from soap with water. The water solution was mixed with the main bulk of soap and the fatty acids were liberated by treatment with dilute sulphuric acid. The mixed acids were subjected to the usual procedure of lead salt, alcohol and ether separation. The resulting fractions were converted into methyl esters and fractionally distilled under a reduced pressure of 0·2 mm

TABLE II.

Materials.	Wt.	Percentage.	Sapon. equiv.	Iodine value.	Materials.	Wt.	Precentage.	Sapno. equiv.	Iodine value.
Oil	450 g.	...	291·5	136	S. Solid acids	25·1 g.	6·1	268·6	34·3
Mixed acids	410·2	91·4	280·4	138	Methyl ester of A.	...	...	294·2	145·2
A. Acid from the lead salts soluble in alcohol	210·4	51·3	281·0	148	,, E.	...	...	299·6	143·4
					,, S.	...	...	282·1	33·8
E. Acids from the lead salts soluble in ether	174·6	42·6	286·2	144·6					

TABLE III.

Fractionation of ester A.

	Fractions.	B. p.	Wt.	Sapon. equiv.	Iodine value.	Fractions.	B. p.	Wt.	Sapon. equiv.	Iodine value
F.	F_{11}	60-110°	6·0g.	226	56·8	F_2	146° g.	21·5 g.	294·8	165·4
	F_{12}	110-140	5·0	230	8·2	F_3	146-150	15·5	294·3	168·2
	F_{13}	145	4·5	287	134·5	F_4	150-55	22·4	294·6	158·4
	F_{14}	147-152	7·5	292	150·0	F_5	155-175	13·5	294·7	138·7
	FR	...	4·6	292	138·0	FR	...	10·5	305·2	120·0

TABLE IV.

Fractionation of ester E.

	B. p.	Wt.	Sapon. equiv.	Iodine value.
E_1	78-150°	6·8g.	290·2	126·4
E_2	145-147	8·9	292·6	140·2
E_3	148	45·0	292·8	142·5
E_4	148-152	35·0	296·4	140·4
E_5	154	8·4	296·3	140·0
ER	...	12·5	298 4	125·

TABLE V.

Fractionation of ester S.

	B. p.	Wt.	Sapon. equiv.	Iodine value.
S_1	98-130	2·8 g.	258·2	23·2
S_2	130-140	3·6	275·4	30·4
S_3	145·	2·4	280·0	35·6
SR	...	3·4	304·1	20·5

FR. contained 3·4% of non-saponifiables.

Myristic acid (m.p. 52°), palmitic acid (m.p. 62°). and stearic acid (m.p. 68°) were identified from the various fractions of the solid acids by their mixed melting point with pure samples of these acids. The fractions of the liquid acids A and E were oxidised individually with alkaline permanganate (Lapworth and Moltram, *J. Chem. Soc.*, 1925, 127, 1678), dihydroxystearic acid (m.p. 130°) and two tetrahydroxy acids, one melting at 154° and the other melting at 174°, were identified.

On extracting the oxidation products of fraction F_1. F_2 and E_1 solid saturated acids *e.g.* lauric acid (m.p. 42°), myristic acid (m.p. 52°) and a little palmitic acid (m.p 62°) were identified by their mixed melting point with pure samples. Fraction S_R gave two acids on crystallisation from ethyl acetate, one melting at 71° which was identified to be archidic acid (mixed melting point with an authentic sample) and the other, melting at 75°, was identified to be lignoceric acid by mixed m.p. with pure lignoceric acid. No behenic acid could be isolated from any fraction of this oil.

10·2 G. of freshly prepared fatty acid were brominated in 100 c.c. of ether at about 0° after which it was left overnight in ice–chest. 0·031 G. of solid bromide, melting at 178°, was obtained which is calculated to be 0·108% linolenic acid in the oil.

The component fatty acids in the glycerides of safflower oil, obtained experimentally, are shown in Table VI.

TABLE VI.

	Acid in A. 51·3%	E. 42·6	S. 6·1	% on mixed acids by wt.	mol.%		Acid in A. 51·3%	E. 42·6	S. 6·1	% on mixed acids by wt.	mol.%
Lauric and lower acids	0·39	...	...	0·4	0·6	Archidic & lignoceric acid	...	...	0·45	0·5	0·5
Myristic acid	0·20	0·06	0·85	1·1	1·3	Oleic acid	14·46	15·54	1·75	32·8	32·6
Palmitic acid	0·80	0·20	1·85	2·9	3·2	Linolic acid	35·35	25·80	...	61·1	60·6
Stearic acid	...	...	1·1	1·1	1·1	Linolenic acid	0·1	...	...	0·1	0·1

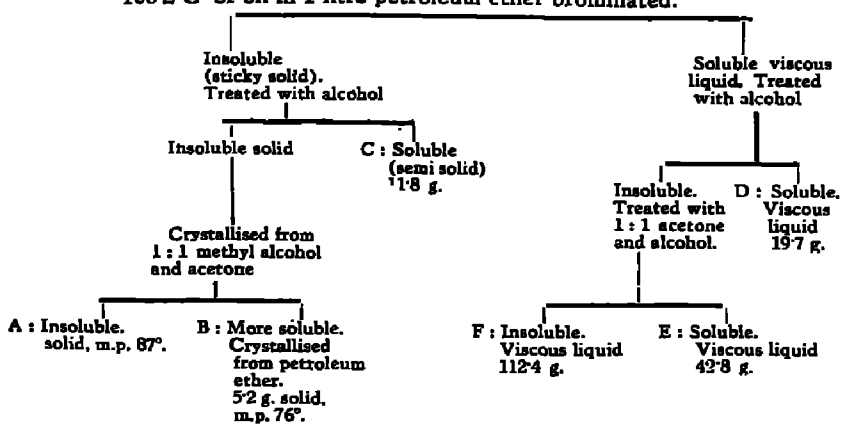
Component Glycerides of Safflower Oil.—Freshly expressed oil was rendered neutral by washing with sodium carbonate solution after which it was filtered through decolourising charcoal. This oil was used for the determination of the composition of the glycerides.

122·8 G. of oil were dissolved in 750 c.c. of acetone and left overnight at 0°. No precipitation occurred. This indicates the absence of fully saturated or disaturated glycerides. This oil was oxidised successively with powdered potassium permanganate after adding another 450 c.c. of acetone. Finally 0·62g. of a neutral product was obtained. On further examination it was found to be only non-saponifiable matter. Consequently this oil does not contain any fully saturated glyceride.

The neutral oil (100·2g.) was dissolved in one litre of petroleum ether and cooled down to −5°to+1°. Bromine was added to it slowly till the whole solution acquired a permanent brown colour. It was then left overnight in refrigerator. The precipitate was filtered and washed off with chilled petroleum ether. The filtrate was washed with sodium thiosulphate solution in order to get rid of bromine. After distilling off the solvent a viscous liquid was obtained which was further separated into different fractions by treating it with alcohol and 1 : 1 alcohol and acetone mixture. The solid was subsequently treated with alcohol and two fractions, one soluble in alcohol and the other insoluble in alcohol, were obtained. The alcohol-insoluble portion was again crystallised from 1 : 1 methyl alcohol and acetone. The portion more soluble in this solvent was crystallised from petroleum ether. A general scheme of separation is given in Table VII.

TABLE VII.

100·2 G. of oil in 1 litre petroleum ether brominated.



All these fractions were debrominated by boiling with zinc dust and hydrogen chloride in ethyl alcohol. The debrominated products were saponified and acids were liberated after extracting the non-saponifiables. 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. As the saturated acids in 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 and the mean molecular weights or the saponification equivalents were determined. The proportions of the unsaturated acids were determined from the saponification equivalent, iodine values and thiocyanogen values.

Fraction A was too small in quantity for all the tests that were carried with the other fractions. Consequently the bromine content of this fraction was determined according to the method of Bacons (*Chem. News*, 1909, 99, 6). (Found : Br, 56·14. Calc. $C_{57}H_{98}O_6Br_2$: Br, 49·63 per cent). The quantity of bromine estimated is more than that calculated for trilinolin and the melting point as well is higher than that observed in the previous case (*J. Indian Chem. Soc.*, 1940, 17, 92) and in fraction B. It might be due to two reasons. First a small quantity of linolenic acid might have formed monolinolenin-dilinolin or a small quantity of the highly unsaturated sterols might have been brominated along with the glycerides to give bromides insoluble in petroleum ether. The quantity was so small that further tests were not possible. As the major portion of this fraction appears to be trilinolin, other considerations have been given up and the whole fraction has been considered to be trilinolin. The analytical results of all the fractions are given in Table VIII.

TABLE VIII.

	A	B	C	D	E	F	Total
Weight in g.	1·2	5·2	11·8	19·7	42·8	112·4	193·1 g.
Saponification equivalent of the acids	...	282·4	272	275·3	282·3	281·6	
Iodine value	...	183·6	122·7	91·8	135·2	149·5	
Thiocyanogen value	...	90·2	62·2	60·1	90·4	90·4	
Weight of the debrominated glycerides	0·51	2·5	6·65	12·4	23·2	57·5	
Free from non-sap. (wt of non-sap.)	0·04	0·38	0·004	0·008	0·45	0·12	
% Glycerides free from non-sap.	0·50	2·3	6·5	12·2	22·2	56·3	
Saponification equivalent of the saturated acids.	...	...	253	248	Trace	...	

From these analytical results the molecular proportions of the various acids in each fraction were calculated. These are given in Table IX.

TABLE IX.

	Mol % of the acids in each fraction.							Mol % of the acids in the fraction on total acids.						
Acids	A	B	C	D	E	F	Mean.	A	B	C	D	E	F	Mean.
Oleic acid	...	..	3	31·1	56·5	34·5	35·09	...	...	0·19	3·8	11·7	19·4	35·09
Linolic acid	100	100	66	35·6	43·5	65·5	58·65	0·5	2·3	4·15	4·3	10·5	36·9	58·65
Saturated acids	...	...	31	33·3	Trace	...	6·26	...	...	2·16	4·1	Trace	...	6·26

The composition of the fatty acids obtained by the bromination of the oil agrees with that obtained by ester fractionation method.

The component glycerides of the safflower oil have been calculated from these results and are given in Table X.

TABLE X.

Fractions.	0·5 A	2·3 B	6·5 C	12·2 D	22·2 E	56·3 F	Total
1. Fully saturated glyceride	Nil	Nil	Nil	Nil	Nil	Nil	Nil
2. Disaturated glycerides	...	...	...	...	...	...	Nil
3. Monosaturated glycerides :							
(*a*) monosaturated dilinolin	...	...	5·8	0·8	...	...	6·6
(*b*) monosaturated oleo-linolin	...	...	0·6	11·4			12·0
4. Tri-unsaturated glycerides :							
(*a*) Dioleolinolin	...	...	...	...	12·9	1·9	63·7
(*b*) Oleodilinolin	...	...	...	...	9·3	54·4	14·8
(*c*) Trilinolin	0·5	2·3	0·1	...	...	...	2·9

The proportion of the various saturated acids in the oil is already known. On the assumption that all the saturated acids have distributed themselves as oleo-linoleo-saturated glycerides and dilinoleo-saturated glycerides in the same proportion as these glycerides exist in the oil, the component glycerides of the safflower oil may be regarded approximately as :—mono-myristo-oleolinolin 2%, monopalmito-oleolinolin 7%, monostearo-oleolinolin 2%, myristodi-linolin 1%, palmitodilinolin 4%, stearo-dilinolin 1%, dioleolinolin 15% and oleodilinolin 63%.

The myristo glyceride contains a little of lauric and other lower acids and stearo glycerides contain little of archidic and lignoceric acids.

The component fatty acids of the Indian safflower seed oil are compared here with those of the two varieties of American (Jamieson and Gertler, *Oil & Fat Ind.*, 1929, 6, No. 4, II ; Vanloon, *Verf. Kronick*, 1937, 10, 80) and one variety of Mid Asiatic oil (Zuckerwanik, *Acta Univ. Asiae. Medic*, 1938. 6 No. 2, 3, 14].

TABLE. XI.

	American		Mid Asiatic.	Indian.		American.		Mid Asiatic.	Indian.
	1.	2.	3.	4.		1.	2.	3.	4.
Saturated acids	6·25	8·6	8·9	6	Linolic	67·4	71·3	39-50	61·1
Oleic	26·2	16·7	34·37	32·8	Linolenic	0·15	3·4	0·5	0·1

Both the samples of the American safflower oils, grown in temperate climate, are richer in the acids having two or three ethylenic linkages, compared to the Mid Asiatic and Indian oils, as expected according to Ivanov's hypothesis (*loc. cit.*). The 2nd sample of the American oil appears to contain exceptionally high percentage of linolic and linolenic acid which may either be due to the different variety of seed or to the difference in climate and soil of the area where it might have been grown.

Received September 29. 1942.

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