CHEMICAL INVESTIGATION OF INDIAN FRUITS

Part II. The Composition of the Oil from the Seeds of Indian Shaddock

By C. J. Dasa Rao, T. R. Seshadri
and
J. Veeraraghaviah
(*From the Department of Chemical Technology, Andhra University, Waltair*)

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As a group the citrus fruits are very important. In the fruit industry, their value depends not only upon the quality of the juice, but also upon the possible utilisation of the by-products such as the peels and seeds. In a previous publication[1] the nature of the bitter principles present in the Indian Shaddock was dealt with. It was pointed out that the seeds are large and form a good percentage of the fruits. They yield about 40% of their weight of oil whose composition has now been studied.

As relevant to the present work it may be stated that Jamieson, Baughman and Gertler[2] investigated the fixed oil from grape fruit seeds obtained in America and found it to contain 26·6–27·6% of saturated acids. The percentage composition of the expressed oil was represented as olein 20·5, linolin 51·0, palmitin 20·1, stearin 7·6, lignocerin 0·1 and unsaponifiables 0·7. Van Loeseke[3] working on some problems in citrus products research found that grape fruit seed oil was rendered palatable by treatment with NaOH and charcoal. A solid at room temperature was obtained by hydrogenation of the oil in the presence of a catalyst. Bubbling air through the oil at elevated temperatures increased the viscosity and drying properties and when it was treated with sulphur chloride the oil yielded a rubber substitute similar to that obtained from cotton seed and maize oils.

The oil that was obtained by petroleum extraction of the shaddock seeds was employed for the present investigation. It was free from any bitterness, was golden yellow in colour and was edible. The mixed fatty acids that were isolated amounted to 90% of the oil and were composed of unsaturated acids 64% and saturated acids 36%. The acids were separated by the Twitchell's lead salt alcohol and ether method. The methyl esters of the liquid acids were fractioned under a reduced pressure of 0·2 mm. and the individual acids identified in each fraction by oxidation with alkaline permanganate according to the method of Lapworth and Mottram and subsequent comparison of the oxidation products with authentic samples.

The percentages of the various acids have been determined from these fractions. The individual liquid fatty acids were also identified and estimated by their bromo-derivatives as described by Eibner and Muggenthaler. The composition of the solid fatty acids was determined by making use of the barium acetate method of Heintz. The fatty acid composition was thus found to be palmitic acid 20·7%, stearic acid 15·3%, oleic acid 55·15%, linolic acid 8·03%, linolenic acid 0·48% and non-saponifiables 0·34%. It follows therefore that the major portion of the unsaturated acids of the shaddock seed oil consists of oleic acid whereas in the grape fruit seed oil linolic acid seems to be the main unsaturated component.

Experimental

1 kg. of the air-dried and powdered seeds were extracted with petroleum ether. 390 g. of a yellow oil was obtained which had the following characteristics:—

Taste not bitter (oil content of seeds)	39%
Specific gravity at 31° C.	0·9086
Refractive Index at 31° C.	1·4645
Saponification value	189·7
Iodine value	92·7
Free fatty acid (% as oleic acid) ..	15·37
Unsaponifiable matter	0·48

140 g. of the oil were treated with alcoholic sodium hydroxide and 126 g. of mixed fatty acids were obtained by treating the soda soap with mineral acid. The mixed acids had a mean molecular weight or saponification equivalent of 277·3 and an Iodine value 94·1.

Separation of solid and liquid acids.—120 g. of the mixed acids dissolved in 600 c.c. of 95% alcohol were refluxed for one hour with 90 g. of lead acetate dissovled in 600 c.c. of 95% alcohol. The lead salts that crystallised on leaving overnight were separated. The acids were liberated by treating separately the alcohol insoluble and soluble lead salts with hydrochloric acid.

	Weight in grams	%	Sap. Eq.	I. V.
Solid acids (lead salts insoluble in alcohol)	43·2	36	268·5	2·42
Liquid acids (lead salts soluble in alcohol)	76·8	64	281·6	104·2

Esterification and Fractionation of the esters of liquid acids.—64 g. of the liquid acids were converted into the methyl esters by boiling with methyl

alcohol in the presence of concentrated H_2SO_4. The resulting esters were rendered free of mineral acids by washing repeatedly with 5% solution of sodium carbonate and afterwards with water. The esters thus obtained weighed 63 g. and had saponification equivalent 295·2 and Iodine value 100·7.

Fractional distillation under 0·2 mm. pressure. Liquid esters 57·3 g.

Fraction	Temp. of still head	Weight of fraction (in grams)	Sap. val.	Sap. Eq.	Iodine number	Non-sap.	Acids identified
1	135–145° C.	18·0	189·8	295·6	100·8	nil	Oleic and linolic
2	147–150° C.	8·0	189·6	295·9	102·3	nil	,,
3	159·0° C.	13·5	189·7	295·7	105·9	nil	Oleic, linolic and linolenic
Residue		17·8	186·5	300·8	103·0	0·3 g.	,,

Corrected saponification equivalent of residue 295·7.

Composition of the fractions by weight

Fraction	Oleic	Linolic	Linolenic	Non-sap.	Total weight in grams
1	15·87	2·13	..	..	18·0
2	6·92	1·08	..	..	8·0
3	11·35	1·95	0·20	..	13·5
4	15·24	2·03	0·23	·30	17·8
Total	49·38	7·19	0·43	0·30	57·3
Calculated on 64% of total acids	55·15	8·03	0·48	0·34	64·0

Identification of the liquid acids in the various fractions was carried out as follows:—Each fraction was saponified and the liberated acids oxidised with potassium permanganate in dilute alkaline solution and the products examined. Fractions 1 and 2 gave dihydroxystearic acid (m.p. 130·5°) and tetrahydroxy stearic acid (m.p. 173°). Fractions 3 and 4 gave dihydroxy-stearic acid and tetrahydroxy-stearic acid in the precipitated acids and in the acid filtrate and acid melting at 204° C. corresponding to Linusic or Hexahydroxy-stearic acid was obtained. The above results of the oxidation clearly indicate the presence of oleic and linolic acids in the first two fractions and oleic, linolic and linolenic acids in the 3rd and 4th fractions.

Examination of the liquid acids by means of their bromo-derivatives.—2·43 g. of the liquid acids were dissolved in ether and the bromides were prepared by using liquid bromine. Separation of the ether insoluble and ether soluble bromides was carried out at −10° C. The ether insoluble bromide was separated and weighed; it was crystalline and melted at 180° C. without darkening during melting, thus showing that it consisted entirely of linolenic acid hexabromide. The ether soluble bromide was washed free of bromine and the ether removed. The residue was dissolved in boiling petroleum ether. On cooling the solution a crystalline precipitate separated and this was weighed. This had a m.p. of 111–13° showing that it consisted of linolic acid tetrabromide. The mother liquor was rendered free of the petroleum ether and the residue dried and weighed as oleic acid dibromide. From the weights of the three fractions the percentages of the various acids were calculated.

	% by Weight on the total bromides	Acid % on liquid acids	Acid % on the total acids	Acids in the fractions
1st fraction, hexabromide .. m.p. 180° C.	2·05	0·75	0·48	Linolenic
2nd fraction, tetrabromide .. m.p. 111–113° C.	27·00	12·60	8·07	Linolic
3rd fraction, dibromide ..	70·95	86·65	54·46	Oleic

Examination of the solid acids.—The solid acids being small in quantity could not be methylated and fractionated. Separation using Barium acetate was effected and the individual fractions were decomposed with hydrochloric acid to liberate the mixed solid fatty acids. The constant of the mixed acids were determined.

Fractional precipitation of the solid acids

Fraction	Weight of fraction in grams	M. P.	Sap. value	Sap. Eq.	Iodine value	Acids identified
1	4·0	64·5	201·6	278·4	2·3	Palmitic and stearic
2	4·0	56·4	214·7	261·3	3·4	,,
3	2·5	56·6	214·5	261·6	2·9	,,

Identification of the individual acids from the fractions was carried out as follows:—The acids liberated from each fraction after crystallisation from

ethyl acetate melted at 69·5° C. and there was no depression in melting point when mixed with pure stearic acid. The acid obtained from the mother liquor when subjected to repeated crystallisation melted at 62·0° C. and the melting point remained the same when mixed with pure palmitic acid. Thus there were only palmitic and stearic acids in the solid acid fraction.

Solid acid distribution by weight

Fraction	Palmitic (in grams)	Stearic (in grams)	Total (in grams)
1	0·80	3·20	4·0
2	3·24	0·76	4·0
3	2·0	0·5	2·5
Total	6·04	4·46	10·5
Calculated on 36% of total acids	20·7	15·3	36

Composition of the fatty acids in the glycerides

Acids	In liquid acids 64%	In solid acids 36%	Total	% by Weight	% on Mol. weight
Palmitic ..	..	20·7	20·7	20·7	22·43
Stearic ..	..	15·3	15·3	15·3	14·94
Oleic ..	55·15	..	55·15	55·46	54·90
Linolic ..	8·03	..	8·03	8·07	7·99
Linolenic ..	0·48	..	0·48	0·48	0·48
Non-Sap. ..	0·34	..	0·34	..	..

Summary

The component fatty acids of the oil obtained from the seeds of Indian shaddock have been examined. It contains very little of unsaponifiable matter and consists of the glycerides of palmitic acid 20·7%, stearic acid 15·3%, oleic acid 55·46%, linolic acid 8·07% and linolenic acid 0·48%.

LITERATURE REFERENCES

1. Seshadri and Veeraraghaviah .. *Proc. Ind. Acad. Sci.*, (A), 1940, 6, 508.
2. Jamieson, Baughman and Gertler .. *Oil and Fat Industry*, 1930, 181.
3. Van Loesele .. *Proc. Fla. Station, Hort. Soc.*, 1933, 38–43.