FIXED OIL FROM *ELETTARIA CARDAMOMUM* SEEDS

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The mixed fatty acids of the fixed oil from *Elettaria cardamomum* seeds have been shown to comprise: caprylic and caproic (0·3%), palmitic (8·4%), stearic (18·3%), Oleic (62·6%) and linoleic (10·5%) acids. The glyceride type distribution of the oil has been determined by Kartha's method.[9] The unsaponifiable matter obtained from the oil has been shown to consist of a sterol probably β-sitosterol.

The cardamoms of commerce are the dried fruits of the reed-like perennial plant *Elettaria cardamomum* Maton, which is classified differently to the natural orders Scitaminaceæ[1,2] and Zingiberaceæ.[3] They are more commonly known as Lesser cardamoms in English, 'Elakki' in Kanarese, 'Chotielachi' in Bengali and Hindi and 'Upakunchika' in Sanskrit. *Elettaria cardamomum* is a native of the moist Ever-green forests of South India, growing wild in the Western Ghats at altitudes lying between 2,500–5,000 ft. Cardamom occurs wild in Ceylon also chiefly in the Ratnapura District and has also been reported in Burmah, China and Malaya.[1] According to 'Ayurveda' the seeds are bitter, cooling, pungent, fragrant, cause biliousness and are useful in asthma, bronchitis, etc. As per 'Unani' literature these are fragrant, tonic to the heart, stomachic, laxative, diuretic and carminative. A number of medicinal uses have been described.[1] The main use of cardamom is for flavouring sweets, puddings, cakes, etc. In India, it is also used as masticatory alone or with *pan*.

Cardamom seeds yield both an essential oil and a fixed oil. Although much work has been done on the chemistry of essential oil obtained from the seeds, no systematic work on the fixed oil obtained from the seeds seems to have been done and reported in the literature. A few characteristics of the oil from the seeds of *E. cardamomum* Minus have been reported by Aug Luhn & Co.[4] Krishnan[5] in the course of investigations on Mysore cardamoms, has observed that the seeds contain 4% of a fixed oil. He has determined the characteristics of the oil as also its fatty acid composition. Subsequent work undertaken in this laboratory on the essential oil from the seeds obtained from Coorg, indicated some variations in the constituents of the oil from those observed by Krishnan.[5] Hence the present investigation on the fixed oil was undertaken. As anticipated, the characteristics and composition of the fixed oil from Coorg cardamoms are somewhat different from those recorded for the fixed oil from Mysore cardamoms.[5]

Essential oil from the dried seeds obtained from Coorg was removed by steam distillation. Carbon tetrachloride extraction then gave 4% of a pale greenish yellow oil with a nutty odour. The oil could not be decolourised by treatment with norite but, however, a pale yellow oil with a thicker consistency could be obtained by chromatographing the oil over alumina, in 75% recovery. The physical and chemical characteristics of the crude as well as the purified oil are noted in Table I.

TABLE I

Characteristics of the oil

No.	Characteristics	Present sample		Aug Luhn & Co.[4]	Krishnan[5]
		Crude	Purified		
1	Ref. index	$n_D^{26°}$ 1·4715	$n_D^{25°}$ 1·4710	..	..
2	Sp. gravity	$d_{26°}^{26°}$ 0·9320	$d_{25°}^{25°}$ 0·9376	$d_{15°}^{100°}$ 0·9030	0·920/23^{c}
3	Melting point of fat	..	..	24·5°	..
4	Acid value	31·98	Nil	4·5 (as oleic acid)	10·84
5	Sap. value	209·00	212·20	206·00	250·30
6	Iodine value	90·60 (Wijs')	89·70	92·00	74·44 (Hubl's)
7	Hehner value	88·5%	91·85%	95·0%	..
8	Sp. rotation in $CHCl_3$	Nil	Nil	..	..
9	Riechert-Miesel value	11·12	..	3·60	..
10	Polenske value	1·45	..	..	..
11	Acetyl value	8·8	..	..	..
12	Unsaponifiable matter	5·87%	Nil	0·35%	4·0%

Component acids of the oil.—The mixed acids (saponification equivalent 276·7; iodine value 86·3) obtained from the oil was resolved into 29·6% solid (saponification equivalent 270·8; iodine value 9·5) and 70·4% liquid (saponification equivalent 280·5; iodine value 97·02) acids by Twitchell's lead salt separation.[6] The methyl esters of the solid as well as the liquid acids were fractionated separately using a 14" indentured column and several fractions were collected. The iodine and saponification values of all the fractions were determined. The fractionation data of the methyl esters is given in Tables II and III.

TABLE II

Fractionation data of methyl esters of solid acids

Weight of ester distilled: 9·05 g.

	Fractions				
	S_{I}	S_{II}	S_{III}	S_{IV}	S_{V}
Boiling point (°C.)	160–80/7 mm.	180–82/7·5 mm.	180–81/6·5 mm.	187–90/7 mm.	Residue (Temp. falling)
Weight (g.)	0·55	1·51	4·83	1·43	0·50
Corrected weight (g.)	0·56	1·55	4·96	1·47	0·51
Iodine value	..	8·48	10·08	14·80	..
Sap. value	205·7	198·4	192·2	190·1	188·4

TABLE III

Fractionation data of methyl esters of liquid acids

Weight of ester distilled: 29·01 g.

Fraction	Boiling point (°C.)	Refractive Index at 22°	Weight (g.)	Corrected Weight (g.)	Iodine value	Saponification value
L_{I} ..	upto 170/4 mm.	1·4570	0·69	0·71	137·5	204·6
L_{II} ..	170–4/4 mm.	1·4570	1·92	1·95	114·8	196·8
L_{III} ..	174–5/4 mm.	1·4532	2·00	2·08	107·8	192·4
L_{IV} ..	173–5/3 mm.	1·4525	3·55	3·64	98·45	189·6
L_{V} ..	175–6/3 mm.	1·4538	10·64	10·90	98·20	190·0
L_{VI} ..	176–9/3 mm.	1·4560	9·00	9·22	90·10	191·2
L_{VII} ..	Residue (Temp. falling)	1·4861*	0·50	0·51	85·95	190·1

* Residue was coloured.

The percentage composition of the mixed acids of the oil, as computed from fractionation data is given in Table IV.

Palmitic and stearic acids were identified in the solid acids by their melting points and also by the melting point of their anilides (palmitic acid m.p. 62°; its anilide m.p. 90–1°; stearic acid m.p. 69°; its anilide m.p. 92–3°). Mixed melting points of the acids with authentic samples were not depressed proving their identity. Palmitic acid (m.p. 62°) was obtained from fraction S_{I} only. Stearic

TABLE IV

Composition of mixed acids

Acid	Present sample		Krishnan[5]
	Wt. %	Mole %	Wt. %
1. Saturated acids:			
(*a*) Caprylic and caproic	0·3	0·64	..
(*b*) Capric	..	..	4·4
(*c*) Palmitic	8·36	8·97	24·3
(*d*) Stearic	18·30	18·02	38·0
2. Unsaturated acids:			
(*a*) Oleic	62·59	61·93	25·7
(*b*) Linoleic	10·49	10·45	..

acid (m.p. 68–9°) was isolated from all the fractions. The absence of any other acids above stearic acid was confirmed by repeated crystallisation of the acid obtained from fraction S_{V}, when the melting point of the acid did not rise above 69°.

The presence of oleic and linoleic acids in the liquid acids was confirmed by bromination[7] and oxidation[8] of the liquid acids. Bromination of the liquid acids gave in addition to tetra-bromostearic acid (m.p. 113–4°) and dibromostearic acid (liquid), a solid (m.p. 173–5°) probably hexa-bromostearic acid. The bromination of acids obtained from fractions L_{I} to L_{VII} was carried out separately in the same way. Ether insoluble bromide (m.p. 173–5°) in minute quantities was obtained from fraction L_{I} only. Fractions L_{I} to L_{V} gave varying amounts of tetra- and di-bromostearic acids, whereas fractions L_{VI} and L_{VII} gave only di-bromostearic acid, as indicated by bromine estimation. However, oxidation of liquid acids gave only tetra-hydroxystearic acid (m.p. 169–70°) and dihydroxystearic acid (m.p. 131–2°) but no hexahydroxystearic acid. Oxidation of acids from L_{I} to L_{VII} did not give any hexahydroxystearic acid. Hence the presence of linolenic acid in liquid acids is rather doubtful.

Component glycerides of the oil.—The types of glycerides present in the oil has been estimated by acetone-acetic acid-permanganate oxidation of the neutral oil by Kartha's method.[9] The GS_3 content of the oil was determined by crystallisation of the oil at 25–6° as described by Kartha.[9] The percentages of the different types of glycerides as estimated by the above method and also computed from the fatty acid composition and GS_3 content of the oil according to Kartha's hypothesis are noted in Table V.

TABLE V

Types of glycerides present in the oil

Glycerides	Experiment		Kartha's hypothesis	
	Wt. %	Mole %	Wt. %	Mole %
1. GS_3 ..	0·60	0·62	0·60	0·62
2. GS_2U ..	23·42	23·68	17·94	18·16
3. GSU_2 ..	43·84	43·87	43·37	43·44
4. GU_3 ..	32·10	31·79	38·09	37·76

Unsaponifiable matter from the oil.—The unsaponifiable matter from the oil (about 5%) answered the characteristic Liebermann-Burchard test for sterols. Hence the present sample differs from the Mysore variety in this respect also, since Krishnan[5] has reported the absence of sterol in the oil. The sterol isolated through its digitonide melted at 136–7° and its acetyl derivative melted at 126–7°. Hence it may probably be β-sitosterol (β-sitosterol[10]; m.p. 138–9°; its acetyl derivative m.p. 127–8°). For want of enough material, the molecular rotation of the sample could not be determined. Free sterol (m.p. 136–7°) could also be obtained from the oil in about 0·2% by chromatographing the oil over alumina.

Two other compounds, *viz.*, a solid melting at 53–7° (0·2 g.) and a thick pleasant smelling liquid (b.p. 75–9°/4 mm., 2·8 g.) were also obtained in accordance with Krishnan's observation.[5] Since the quantity of the material on hand was small, further examination could not be carried out.

EXPERIMENTAL

Extraction of oil.—Extraction of the dry " essential oil-free " powdered seeds (20 mesh–20 lb.) was carried out in a modified soxhlet apparatus in 10 lb. lots using carbon tetrachloride as solvent. The carbon tetrachloride extract gave a dark greenish yellow oil (245 g.). (Percentage of oil obtained from the seeds when extracted in 10 lb. lots was 2·8%. Percentage of oil obtained from the seeds when extracted in 500 g. lots was 4%).

Purification of oil by adsorption over alumina.—The above oil (10 g.) dissolved in carbon tetrachloride (20 c.c.) was adsorbed over a column of alumina (100 g.) and eluted with the same solvent (about 300 c.c.) till no more of oil was recovered. On distilling off solvent a pale yellow viscous oil (7·2 g.) was obtained.

Preparation of mixed fatty acids.—The oil (100 g.) was saponified with alcoholic potash. The dry powdered soap was then extracted with ether to remove the unsaponifiable matter. The free acid was then liberated by acidification with dilute hydrochloric acid when 83·0 g. of mixed fatty acids were obtained.

Twitchell's lead salt separation of mixed fatty acids.[6]—The above mixed fatty acids (62·5 g.) were dissolved in (400 c.c.) boiling ethanol. A boiling solution of neutral lead acetate (60 g.) in ethyl alcohol (400 c.c.) containing 1% glacial acetic acid was added to the former solution with stirring. The resulting mixture was boiled well and allowed to stand at 15° for 24 hours. The insoluble lead salt was filtered and washed thoroughly with alcohol and dried. This was decomposed with dilute nitric acid, when 18·2 g. of pale red solid acids were obtained.

Alcohol was distilled off from the filtrate. The residue consisting of soluble lead salts was taken up in ether and decomposed with dilute hydrochloric acid. The ether solution was then washed free from mineral acid, dried over anhydrous sodium sulphate and filtered. On removing ether completely 44·0 g. of pale red liquid acids were obtained.

Fractionation of methyl esters of solid and liquid acids.—Methyl esters of the solid (9·05 g.) as well as the liquid (29·0 g.) acids, prepared from the corresponding acids, were separately distilled *in vacuo* using a 14″ indentured fractionating column. The distillation of methyl esters of solid acids started at 160°/7 mm. and that of the liquid acids at 155°/4 mm. and several fractions were collected at different temperatures.

Bromination of liquid acids.—Bromination of liquid acids (2·0 g.) dissolved in anhydrous ether was carried out according to the method of Jamieson and Baughman,[7] when 0·05 g. of ether insoluble bromide (m.p. 173–5°), 0·2 g. of ether soluble, petroleum ether insoluble bromide (m.p. 113–4°) and 2·95 g. of petroleum ether soluble bromide were obtained. The bromine content of the residue as estimated by Stepanow's method was 38·5%.

Oxidation of liquid acids.—The oxidation of liquid acids (3·0 g.) was carried out according to the method of Sullivan and Bailey,[8] when 3·3 g. of hydroxy acids were obtained. This was extracted in a glass soxhlet apparatus with ether. The residue from the ether extract was thrice crystallised from ethyl acetate when pure di-hydroxystearic acid (m.p. 131–2°) was obtained. The residue left after ether extraction (m.p. 145–50°) was thrice crystallised from glacial acetic acid, when a small quantity of an acid melting at 168–70° was obtained, indicating to be tetra-hydroxystearic acid. Further purification could not be carried out since the quantity of the material left after the third crystallisation was very small. The filtrate from the original precipitate of the oxidised acids was neutralised and concentrated *in vacuo* to about 50 c.c., when no hexa-hydroxystearic acid was obtained.

The acid obtained from fractions L_{I} to L_{VII} were oxidized in the same way. Di-hydroxystearic acid in large quantities and tetra-hydroxystearic acid in traces were obtained. No hexa-hydroxystearic acid could be isolated from any fraction.

Acetone-acetic acid-permanganate oxidation of oil.[9]—The neutral oil (4·36 g). dissolved in dry acetone (200 c.c.) containing glacial acetic acid (12 c.c.) was oxidized with potassium permanganate (35–40 g.). After the oxidation, acetone was distilled off and the residue was decolourised with sodium bi-sulphite and dilute sulphuric acid. The organic matter was then extracted with ether when 3·95 g. of a residue of oxidized products was obtained.

The above residue was subjected to magnesium sulphate precipitation. From the precipitated magnesium salts, 2·1 g. of a mixture of azelaoglycerides was obtained by acidification. The free acid obtained from this residue by hydrolysis was subjected twice to Bertram's separation[11] when 1·0 g. of saturated acids with a saponification equivalent of 272 and an iodine value of 1·2 were obtained. The filtrate from the magnesium salt precipitation of the oxidized fat, on acidification gave 1·3 g. of a residue. This was hydrolysed and the isolated acids were subjected to Bertram's separation as before, when 0·2 g. of saturated acids with a saponification equivalent of 270 was obtained.

Estimation of GS_3 in the oil.—The neutral oil (4·1 g.) was dissolved in dry acetone (15 c.c.) and the solution held at room temperature (25–6°) for 3 days. The separated solid was filtered and crystallised from acetone under the same solvent ratio, time and temperature. The residue, on vacuum drying, weighed 0·03 g. and this had no iodine value as determined by hydrogenation.

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