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Seed Oils from Cassia Fistula, C. Occidentalis, and C. Tora (Indian Varieties)[1]

M. O. FAROOQ, M. A. AZIZ, and M. S. AHMAD, Department of Chemistry, Muslim University, Aligarh, India

THE CHEMICAL CHARACTERISTICS of the seed oils of three Cassia varieties have been previously recorded. The oil of *C. occidentalis* from the Islands of St. Martins was partly analyzed by Steger and van Loon (17), that of *C. tora* from Indian sources by Manjunath and Jois (14), and that of *C. fistula* of the Sudanese variety by Grindley (5). Chrysophanic acid (4,5-dihydroxy-2-methyl anthraquinone), which has medicinal value, was found by Elborne (4) in the oil from *C. tora* seeds.

The seeds of this family are not known as oil-bearing; they contain mainly carbohydrate as reserve material besides some protein whereas their oil content is small. Some of these oils are used in medicine. Because the recorded data about these oils were fragmentary and incomplete, the present study using methyl-ester fractionation technique was undertaken.

Experimental

The seeds for the present investigations were collected a) *C. fistula* in the vicinity of the Aligarh University and b) *C. occidentalis* and c) *C. tora* from the Barabanki District, U. P. Extraction of the dried and finely crushed seeds with petroleum ether (b.p. 60–80°) in a specially modified Soxhlet apparatus gave 3%, 2.8%, and 5.0% brownish yellow oils, respectively.

In Table I are recorded the physical and chemical constants found for these oils as compared to values reported by other workers.

Fatty acids were isolated in yields of 81.2%, 87%, and 81.4% by successively saponifying the oil with alcoholic potassium hydroxide, removing the unsaponifiable matter by extraction with ether, and acidifying with sulphuric acid. Resins were removed from the acids according to the method described by Lewkowitsch (11) in yields of 1.3%, 1.0%, and 1.5%.

The fatty acids were separated into liquid and solid fraction by the lead salt alcohol method (6). Yields and compositions of the fractions are summarized in Table II.

TABLE II

Fatty Acids from Cassia Oils

Seed	*C. fistula*	*C. occidentalis*	*C. tora*
Total fatty acids			
Iodine value	115.5	114.5	106.1
Thiocyanogen value	74.6	74.0	66.7
Saponification equivalent	289.3	283.0	287.3
Liquid fatty acids			
Yield, % of total	79.1	74.9	73.8
Iodine value	143.7	151.3	142.6
Thiocyanogen value	84.0	......	......
Saponification equivalent	280.5	280.5	284.8
Solid fatty acids			
Yield, % of total	20.9	25.1	26.2
Iodine value	4.6	3.8	3.2
Saponification equivalent	289.4	287.8	274.4
Saturated acids (Bertram method) (2)			
Yield, % of total	19.4	24.0	25.4

The total fatty acid fractions were brominated by the method of Eibner and Mugganthaler (13). Bromo-derivatives having the following melting points were obtained:

Fatty acids	Hexabromo- m.p.	Tetrabromo- m.p.	Dibromo-
C. fistula	......	114–15°	liquid
C. occidentalis	178–80°	115–16°	liquid
C. tora	......	114–15°	liquid

The same products were obtained by bromination of liquid fatty acid fractions.

Methyl esters were prepared from the liquid and solid fatty acid fractions by the method of Hilditch (7) and were fractionally distilled under reduced pressure from a Claisen's flask attached to a Kon-type vacuum fractionation receiver (18).

Iodine values and saponification equivalents of the ester fractions were determined. These data were used in calculating fatty acid compositions of the esters (8).

Identities of the fatty acids were established 1) by isolating the saturated acids from samples used for

TABLE I

Physical and Chemical Constants of Cassia Oils

Seed	*C. fistula*		*C. occidentalis*		*C. tora*	
Origin	India	Africa (5)	India	St. Martins (17)	India	India (14)
Oil yield, %	3.0	2.04	2.8	2.3	5.0	5.0
Specific gravity	0.9112^{20}	....	0.9166^{32}	....	0.9012^{32}	0.8969^{25}
Refractive index	1.4672^{40}	1.4668^{40}	1.4714^{32}	1.477^{15}	1.4672^{32}	1.4669^{25}
Saponification value	184.2	184.4	176.1	178.7	163.4	154.2
Acetyl value	9.2	....	....	....	11.2	9.6
Acid value	2.9	....	5.4	10.2	4.2	10.8
Iodine value (Hanus)	109.3	94.5	110.3	113.9	91.3	90.7
Thiocyanogen value	66.6	63.2	72.6	78.2	58.2	....
Unsaponifiable, %	5.7	5.4	8.3	7.35	5.7	5.4
Protein, %	2.7	....	14.72	....	19.84	....

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[1] The work described in this paper was carried out in the Prince of Wales Chemical Laboratories, Muslim University, Aligarh, India.

TABLE III

Methyl Esters of Fatty Acids from *C. Fistula* Oil

Fraction	Weight g.	Distillation temperature at 2 mm. Hg pressure	Iodine value	Saponification equivalent	Calculated Composition (g.)		
					Palmitate	Oleate	Linoleate
L_1	4.72	162°	135.0	289.7	0.26	1.90	2.56
L_2	4.65	162–64°	142.1	292.5	......	1.60	3.05
L_3	2.50	164–66°	138.8	293.8	......	0.96	1.54
L_4 (10)	2.40	residue	107.5	294.4	......	0.92	1.48
	14.27				0.26	5.38	8.63
		at 3 mm. Hg		Corrected saponification equivalent (3)	Palmitate	C_{18}-mono-unsaturated	Lignocerate
S_1	2.60	162°	2.2	270.6	2.53	0.07	......
S_2	3.00	162–63°	3.6	272.5	2.86	0.13	0.01
S_3	3.13	163–64°	5.53	288.04	2.34	0.20	0.62
S_4	2.20	residue	8.2	378.0	0.06	0.21	1.92
	10.93				7.79	0.60	2.55

determination of saponification equivalents of methyl ester fractions and 2) by isolating hydroxy acids from the oxidation of methyl esters of liquid fatty acids with permanganate by Hazura's method (12). The saturated and hydroxy acids were crystallized from alcohol. In the case of *C. occidentalis* fatty acids the proportions of oleic, linoleic, and linolenic acids were determined thiocyanometrically (15) because when linolenic acid occurs in mixture with other C_{18} mono- and diethenoid acids, the methyl ester fractionation method does not give reliable results (9). Saturated acids from this oil were purified by the Bertram oxidation method (2) and were then esterified and fractionated.

Methyl ester fractionation data are summarized in Tables III, IV, and V.

From the products of the oxidation of III-L there were isolated: palmitic acid, m.p. 59–61°, no depression of melting point when mixed with authentic sample; tetrahydroxystearic acid, m.p. 170–2°; and dihydroxystearic acid, m.p. 130–2°. From III-S the following acids were identified: palmitic acid, m.p. and mixed m.p. 61–63°; and lignoceric acid, m.p. and mixed m.p. 80–81°, mol. wt. 366.8. From IV-S were isolated: palmitic acid, m.p. and mixed m.p. 60–62°; and lignoceric acid, m.p. and mixed m.p. 78–80°, mol. wt. 367. From the products of oxidation V-L there were isolated: palmitic acid, m.p. and mixed m.p. 60–62°; tetrahydroxystearic acid, m.p. 170–72°; and dihydroxystearic acid, m.p. 130–2°. From V-S were identified: palmitic acid, m.p. and mixed m.p. 60–62°; lignoceric acid, m.p. and mixed m.p. 79–81°, mol. wt. 366.

Isolation of Chrysophanic Acid (4,5-dihydroxy-2-methyl anthraquinone). A solution of 50 g. of oil of *C. tora* in petroleum ether was extracted thoroughly with 2% aqueous caustic soda until the alkaline extract was colorless. The alkaline extract was washed repeatedly with ether in order to remove completely the emulsified oily matter. A stream of carbon dioxide was passed through the alkaline solution until no further change was observed. The yellow precipitate was dissolved in chloroform, washed free of alkali and soap, and dried over anhydrous sodium sulphate. Removal of sodium sulphate and chloroform yielded a yellow mass (0.46 g.). Successive crystallization of this crude product from benzene, acetone, ether, and alcohol yielded 0.3 g. of chrysophanic acid, m.p. 196–96.5°.

TABLE IV

Methyl Esters of Saturated Acids from *C. Occidentalis* Oil

Fraction	Weight g.	Distillation temperature at 2 mm. Hg pressure	Saponification equivalent	Calculated composition (g.)	
				Palmitate	Lignocerate
S_1	3.90	160°	270.6	3.90	......
S_2	3.15	160–62°	274.8	2.87	0.28
S_3	3.10	162–64°	284.6	2.57	0.53
S_4	2.75	Residue	322.6	1.24	1.51
	12.90			10.58	2.32

The oil of *C. occidentalis* on similar treatment gave only traces of chrysophanic acid.

Discussion

Cassia seeds contain 2.0 to 5.0% of semi-drying oil. All of these so far examined are contaminated with

TABLE V

Methyl Esters of Fatty Acids from *C. Tora* Oil

Fraction	Weight g.	Distillation temperature at 2 mm. Hg pressure	Iodine value	Saponification equivalent	Calculated composition (g.)		
					Palmitate	Oleate	Linoleate
L_1	7.2	160°	134.6	290.3	0.4	2.93	3.87
L_2	7.0	160–62°	140.2	292.6	......	2.56	4.44
L_3	3.6	162–64°	142.3	294.6	......	1.23	2.37
L_4(10)	3.8	Residue	110.6	295.8	......	1.30	2.50
	21.6				0.4	8.02	13.18
				Corrected saponification equivalent(3)	Palmitate	C_{18} mono-unsaturated	Lignocerate
S_1	7.3	158°	1.3	270.6	7.19	0.11	......
S_2	8.5	158–60°	1.6	271.3	8.21	0.16	0.13
S_3	4.5	160–62°	3.4	284.4	3.58	0.18	0.74
S_4	2.3	Residue	5.8	377.8	0.06	0.15	2.09
	22.6				19.04	0.60	2.96

TABLE VI
Composition of Total Fatty Acids

Analytical method	Fractionation, %	Thiocyanometric, %	Thiocyanometric, %
Cassia fistula			
Origin	India	India	Africa (5)
Oleic	30.70	34.23	31.90
Linoleic	48.09	46.90	39.00
Palmitic	16.01	18.87	29.10
Lignoceric	5.20		
Cassia occidentalis			
Origin	India	India	St. Martins (17)
Oleic	......	31.60	34.80
Linoleic	......	38.10	35.70
Linolenic	......	6.30	7.10
Palmitic	19.68	24.00[a]	22.40
Lignoceric	4.32		
Cassia tora			
Origin	India	India	India (14)
Oleic	28.12	27.20	......
Linoleic	45.02	45.20	......
Palmitic	23.43	27.60	......
Lignoceric	3.43		......

[a] Bertram (2).

small quantities of resins. The data on fatty acid compositions determined in the present study compare well with the data previously reported (Table VI) and show that these oils differ from other seed oils in containing lignoceric acid (1, 16, 14) but little (1) or no stearic acid (16, 14).

Cassia oils contain about the same proportion of linoleic acid as do soybean and linseed oils. It was observed that there is more linoleic acid and a smaller amount of saturated acids in the Indian than in the African varieties of *Cassia fistula* oils. Although the oil content of the Indian variety of *C. occidentalis* seed is slightly higher than that of the St. Martins Island variety, the properties of the oils are the same.

The oil from *C. tora* which contains chrysophanic acid may find use as a purgative or intestinal disinfectant. The soap may be useful in the treatment of skin diseases, such as ringworm and itches.

Summary

Fatty acids from oils of Indian varieties of *C. fistula, C. occidentalis,* and *C. tora* were fractionated by the lead salt-alcohol and methyl ester distillation methods. Compositions were calculated from the iodine values and saponification equivalents of the ester fractions. Identities of saturated acids were established by determining the properties of the recrystallized acids. Unsaturated acids were identified as the bromo- and hydroxy-derivatives.

Cassia fistula, C. occidentalis, and *C. tora* oils were found to contain the following percentages of fatty acids, respectively: palmitic, 16.0, 19.7, 23.5; lignoceric, 5.2, 4.3, 3.4; oleic, 30.7, 31.6, 28.1; and linoleic, 48.1, 38.1, 45.0. In addition, *C. occidentalis* oil contained 6.3% of linolenic acid.

Chrysophanic acid was isolated in yield of 0.6% from *C. tora* oil, but only traces were obtained from *C. occidentalis* oil.

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Preliminary Report on a Rapid Method of Evaluating Detergency by Means of an Ultrasonic Transducer

JOSEPH C. SHERRILL, College of Household Arts and Sciences, Texas State College for Women, and W. CRAIG WHITE, Chemicals and Plastics Division, Quartermaster Research and Development Center, Natick, Massachusetts

THERE HAS BEEN a serious need for a highly objective but rapid method for obtaining comparative detergency data on compounds and procedures so that these could be evaluated with a high degree of accuracy and precision.

It is believed that this need is being met as a result of the work described in this report. An ultrasonic transducer, designed and built by Clevite-Brush Company, Cleveland, Ohio, has been adapted in the laboratories of the first-named author to the purpose of removing soil from standard soiled surfaces in a short period of time, under circumstances in which the actual energy output of the transducer is known. This energy output can be related to the amount of soil removed from an exposed surface.

The ultrasonic transducer, with the adaptations as applied in converting the original device to the purpose in hand is suitable for determining the removal of soil on a quantitative basis from the following types of surfaces: a) various textiles, b) metallic surfaces, c) ceramics, and d) plastics.

Experimental Procedure

The Cone Transducer. Work has been directed in these laboratories toward the investigation of sound transducers of several types. The development most applicable to this study was found to be the cone transducer, after examination of the operational characteristics of four other transducer types. Investigations into the magnitude of energy required