Technical

Characteristics and Composition of Six Malvaceae Seeds and the Oils

K. SUNDAR RAO and G. LAKSHMINARAYANA,* Regional Research Laboratory (CSIR), Hyderabad - 500 007, India

ABSTRACT

The seeds of Sida veronicifolia Linn., syn. S. bumilis cav., S. cordifolia Linn., S. ovata Forsk., S. mysorensis W & A., syn. S. urticaefolia W & A, S. rhombifolia var. retusa Masters and Abutilon crispum Medik. (Malvaceae) contained 15.5%, 11.5%, 12.1%, 13.2%, 20.2% and 12.5% oil, and 15.0%, 14.1%, 17.3%, 13.6%, 12.6% and 18.4% protein, respectively. Linoleic acid predominated (54.9-69.4%) as the fatty acid of all the oils, and malvalic (1.3-11.4%) and sterculic acids (0.4-1.1%) were significant.

INTRODUCTION

Seed oils of many species of the Malvaceae family are reported (1) to contain cyclopropene fatty acids (CPFA), which have adverse biological activity (2,3). During our search for newer oilseeds for augmenting oil resources, we have come across the following 6 species of Malvaceae: Sida veronicifolia Linn., syn. S. humilis cav., S. cordifolia Linn., S. ovata Forsk., S. mysorensis W & A., syn. S. urticaefolia W & A., S. rhombifolia var. retusa Masters and Abutilon crispum Medik. Different parts of these plants are used in indigenous medicine (4-6). The characteristics and composition of the seeds, as well as the oils extracted from them, are reported here for the first time.

EXPERIMENTAL METHODS

The physicochemical characteristics of seeds and oils were determined according to the Official and Tentative Methods of the American Oil Chemists' Society (7). The oils were examined for ultraviolet (UV) absorption in CCl₄ on a Beckman 26 UV-Visible spectrophotometer, for infrared (IR) absorption as a liquid film on a Perkin-Elmer 221 spectrometer and for proton nuclear magnetic resonance (¹H-NMR) in CCl₄ on a Varian A-60A instrument with tetramethylsilane as the internal standard (8-10).

The oils were treated with diazomethane to esterify the free fatty acids, and then with methanolic sodium methoxide (1.0%) to convert glycerides to methyl esters according to the procedure described by Schneider et al. (11). The oils, as well as the methyl esters, were qualitatively examined for the presence of hydroxy, epoxy and CPFA components by the sulfuric acid turbidity test (12), Fioriti's picic acid test (13) and the Halphen test (7).

Epoxy esters were separated from nonepoxy esters by preparative thin layer chromatography (TLC) on 0.8 mm layers of Silica gel G, using a mixture of petroleum ether (40-60 C) and peroxide-free diethyl ether (80-20, v/v) as developer and 2',7'-dichlorofluorescein as spraying reagent. The bands of epoxy (R_f 0.65) and nonepoxy (R_f 0.91) esters were detected in UV light. Authentic standards of methyl epoxystearate and methyl esters of *Sterculia foetida* seed oil were used for reference. The bands were separately scraped off and extracted with diethyl ether. The epoxy esters were estimated using methyl heptadecanoate as internal standard by gas liquid chromatography (GLC) after conversion, first to hydroxy-methoxy esters by refluxing with methanolic BF_3 , and subsequently to trimethylsilyl ethers by treating with hexamethyldisilazane and trimethylchlorosilane in pyridine (14).

The nonepoxy methyl esters, which include CPFA esters, were treated according to the method of Schneider et al. (11) with anhydrous methanol saturated with silver nitrate for 20 hr at ambient temperature to convert CPFA esters into stable ether and keto derivatives for GLC analysis. GLC analysis was carried out using a Hewlett-Packard 5840A unit fitted with a flame ionization detector (FID) and a data processor. Nitrogen was used as carrier gas (35 mL/min). The column, injection port and detector were maintained at 200 C, 250 C and 300 C. A glass column (0.6 m \times 6 mm) packed with 5% SE-30 on Chromosorb W, 60-80 mesh and a glass column (1.8 m \times 6 mm) packed with 10% Silar 10C on Chromosorb W HP; 80-100 mesh were used for the analysis of epoxy ester derivatives and nonepoxy esters containing CPFA derivatives. The peaks were identified using authentic fatty acid methyl esters, including CPFA esters from S. foetida oil. Estimation of CPFA derivatives and dihydrosterculic acid was described previously (15).

RESULTS AND DISCUSSION

The characteristics of the seeds and oils are given in Table I. All the seeds analyzed are of small size, as indicated by 100-seed weight and volume. The oil and protein contents were not high, compared with those of conventional oilseeds. None of the plant species studied appear promising as sources of oil and protein. The contents of unsaponifiable matter in the oils were slightly higher than in conventional oils. The oils from all the samples responded positively to the Halphen and Fioriti tests indicating the presence of cyclopropene and epoxy fatty acids. The IR spectra showed a band at 1008 cm⁻¹ and the NMR spectra a signal at 9.2 τ , characteristic of the cyclopropene moiety. The turbidity test, as well as IR spectra, did not show the presence of hydroxy fatty acids. The UV and IR spectra showed no conjugated or *trans* unsaturation.

The fatty acid compositions are presented in Table II. Linoleic acid was the predominant fatty acid (54.9-69.4%), followed by palmitic acid (15.7-21.8%), in all the oils. Total CPFA content ranged from 2.2% to 12.5%. In each case, a greater amount of malvalic acid was present than sterculic acid, especially in *S. veronicifolia* seed oil. The seed oils of *S. veronicifolia* and *A. crispum* contained 0.2% and 0.8% dihydrosterculic acid, and the other seed oils had only trace quantities (<0.1%). This acid was a suggested intermediate in the biosynthesis of malvalic and sterculic acids in seedlings of some species of the Malvaceae family (16). Epoxy acid was present in 0.4% concentration in *A. crispum* fatty acids, and trace quantities were present in other seed fatty acids.

In malvaceae seed oils, linoleic acid generally predominates, followed by oleic and palmitic acids, and CPFA is present in significant quantities (1,17). The dihydroderivatives of CPFA and epoxy fatty acids also occur in small quantities in some species. The fatty acid compositions of 6 seed oils of the Malvaceae family studied in this investigation fit into this general pattern. The pattern observed with the 5 Sida species is similar to that of S. grewioides (18),

^{*}To whom correspondence should be addressed.

TABLE I

Physicochemical Characteristics of Malvaceae Seeds and Oils

	S. veronicifolia	S. cordifolia	S. ovata	S. mysorensis	S. rhombifolia	A. crispun
Seed						
Weight of 100 seeds (g)	0.20	0.32	0.26	0.22	0.23	0.24
Volume of 100 seeds (mL) ^a	1.2	1.0	1.0	0.8	0.7	1.0
Moisture (%)	5.4	5.1	4.2	4.6	5.3	4.3
Oil (% ^b)	15.5	11.5	12.1	13.2	20.2	12.5
Protein (% ^b)	15.0	14.1	17.3	13.6	12.6	18.4
Ash (% ^b)	3.9	3.7	3.4	3.5	4.5	3.6
Dil						
Refractive index at 25 C	1,4727	1,4691	1,4724	1.4726	1.4746	1.4684
Acid value	5.8	4.8	3.3	5.9	6.8	6.3
Saponification value	182.7	185.8	189.6	184.9	184.2	184.3
Iodine value	109.5	115.9	125.5	121.4	109.1	118.4
Unsaponifiable matter (%)	5.1	4.3	2.7	4.9	4.8	4.0

^aBy displacement in either water or n-hexane.

bDry basis.

TABLE II

Fatty Acid Composition (Area Percentage) of Malvaceae Seed Oils

Fatty acid	S. veronicifolia	S. cordifolia	S. ovata	S. mysorensis	S. rhombifolia	A. crispum
Lauric	0.0	0.0	0.4	1,1	1.5	0.0
Myristic	0.2	0.2	0.3	0,2	0,3	0.2
Palmitic	21.8	18.2	16.5	15.9	16.7	15.7
Stearic	4.2	4.6	2.4	2.7	2,6	2.7
Oleic	5.4	10.7	6.8	10.9	8,3	12.2
Linoleic	54.9	62.8	69.4	66.0	65.5	61.2
Arachidic	0.8	0.6	1.9	0.9	1,7	1.0
Malvalic ^a	11.4	2.2	1.8	1.3	2.1	4.5
Sterculic ^a	1.1	0.6	0.4	0.9	0.8	1.3
Dihydrosterculic	0.2	Trace	Trace	Trace	Trace	0.8
Epoxyb	Trace	Trace	Trace	Trace	Trace	0.4

^aEther plus keto derivatives.

^bTrimethylsilyl ethers of hydroxy-methoxy derivatives.

except that S. veronicifolia seed oil contained an appreciable amount (12.5%) of CPFA. A similar amount of CPFA has been reported in the seed oils of S. acuta and rhombifolia, which, however, contained much less linoleic acid than oleic and palmitic acids (19). The CPFA contain mainly malvalic acid in S. veronicifolia and sterculic acid in S. acuta and S. rhombifolia. The fatty acid composition of A. crispum seed oil resembles that of A. auritum (20), A. indicum (21), A. pannosum (22), A. graveolens (23) and A. pseudocleitoganum (24).

ACKNOWLEDGMENTS

CSIR, New Delhi, awarded a Senior Research Fellowship to K. Sundar Rao. G. Narasimha Rao, Botany Department, Osmania University, Hyderabad, India, identified the plants.

REFERENCES

- 1. Smith, C.R., Jr., in Progress in the Chemistry of Fats and Other Lipids, Vol. XI, Part I, Pergamon Press, New York, 1970, pp. 139-177.
- Phelps, R.A., F.S. Shenstone, A.R. Kemmerer and R.J. Evans, Poult. Sci. 44:358 (1965). 2
- 3. Lee, D.J., J.H. Wales and R.O. Sinnhuber, Cancer Res. 31:960 (1971).
- Chopra, R.N., S.L. Nayar and I.C. Chopra, in Glossary of Indian Medicinal Plants, Council of Scientific and Industrial Research, New Delhi, 1956, p. 227. 4.
- 5. The Wealth of India, Raw Materials, Vol. 9, Council of Scientific and Industrial Research, New Delhi, 1972, p. 326.
- Venkateswarlu, J., P.V. Bhiravamurthy and P. Narasimha Rao, 6.

in The Flora of Visakhapatnam, Andhra Pradesh Academi of Sciences, Hyderabad, India, 1972, p. 28. Official and Tentative Methods of the American Oil Chemists'

- 7 Society, 3rd edn., 1958 (revised 1973), AOCS, Champaign, IL.
- Pitt, G.A.J. and R.A. Morton, in Progress in the Chemistry of Fats and Other Lipids, Vol. IV, Pergamon Press, New York, 8. 1957, pp. 228-278.
- 10.
- O'Connor, R.T., JAOCS 38-648 (1961). Hopkins, C.Y., Ibid. 38:664 (1961). Schneider, E.L., S.P. Loke and D.T. Hopkins, Ibid. 45:585 11. (1968).
- Lakshminarayana, G., Ibid. 45:523 (1968) 12
- 13
- Fioriti, J.A., A.P. Bentz and R.J. Sims, Ibid. 43:489 (1966). Gunstone, F.D., and H.R. Schuler, Chem. Phys. Lipids 15:198 14.
- (1975).Rao, K.S., A.J. Pantulu and G. Lakshminarayana, JAOCS 60-15. 1259 (1983).
- Johnson, A.R., J.A. Pearson, F.S. Shenstone, A.C. Fogerty and 16. J. Giovanelli, Lipids 2:308 (1967). 17. Hilditch, T.P. and P.N. Williams, The Chemical Constitution
- of Natural Fats, 4th edn., Chapman & Hall, London, 1964, pp. 266-271.
- Husain, S., M. Babu, M.U. Ahmad, A.A. Ansari and S.M. 18 Osman, Fette Seifen Anstrichm. 82:29 (1980).
- Ahmad, M.U., S.K. Husain, M. Ahmad, S.M. Osman and R. Subbarao, JAOCS 53:698 (1976). 19.
- Vickery, J.R., Ibid. 57:87 (1980).
- Babu, M., S. Husain, M.U. Ahmad and S.M. Osman, Fette 21. Seifen Anstrichm. 82:63 (1980).
- Kittur, M.H., C.S. Mahajanshetti, K.V.S.A. Rao and G. Lak-22 shminarayana, JAOCS 59:123 (1982).
- Gopalakrishnan, N., T.N.B. Kaimal and G. Lakshminarayana, 23. J. Oil Technol. Assoc. India 15:2 (1983) 24.
- Gaydou, E.M., and A.R.P. Ramanoelina, Fette Seifen Anstrichm. 86:82 (1984).

[Received December 6, 1983]