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FATTY ACID COMPONENTS OF SOME SANTALACEAE SEED OILS*

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Abstract—Seed oils of five species of the family Santalaceae, not studied previously, were examined to determine the nature of the fatty acid components. An acid (or acids) having a conjugated *trans*-enyne group was present in all. Species of *Buckleya* and *Thesium* had also an enediyne component; those of *Geocaulon* and *Jodina* contained a hydroxy acid. *Jodina* had a large proportion of non-hydroxy C-17 acid. Ximenynic acid was the main component of *Santalum yasi* oil. Infrared spectra and other data were obtained for six additional species of Santalaceae. The distribution pattern of acetylenic and other fatty acids in this family is discussed in relation to the classification of the genera.

INTRODUCTION

THE SEED oils of a number of Santalaceae species are rich in acetylenic fatty acids.[1,2] At least one acetylenic acid (Fig. 1) has been found in the seed oil of every species of this family that has been examined so far. There is considerable variation in fatty acid composition among the genera, however, and the presence or absence of a particular acid may constitute a useful chemotaxonomic character.

Stearolic $CH_3(CH_2)_7C{\equiv}C(CH_2)_7COOH$ (I)

Ximenynic $CH_3(CH_2)_5CH{=}CH.C{\equiv}C(CH_2)_7COOH$ (II)

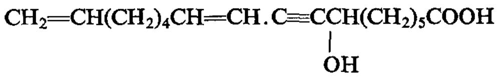
Exocarpic $CH_3(CH_2)_3CH{=}CH.C{\equiv}C.C{\equiv}C(CH_2)_7COOH$ (III)

Pyrulic $CH_3(CH_2)_5CH{=}CH.C{\equiv}C(CH_2)_6COOH$ (IV)

Octadeca-*trans*-11,17-dien-9-ynoic

$CH_2{=}CH(CH_2)_4CH{=}CH.C{\equiv}C(CH_2)_7COOH$ (V)

7-Hydroxyheptadeca-*trans*-10,16-dien-8-ynoic



$$CH_2{=}CH(CH_2)_4CH{=}CH.C{\equiv}C\underset{\displaystyle OH}{\underset{|}{C}}H(CH_2)_5COOH$$ (VI)

FIG. 1. SOME ACETYLENIC ACIDS OF SANTALACEAE SEED OILS

The classification of Santalaceae and related families has offered some difficulties.[3,4] Thus the position of the genus *Exocarpus* has been uncertain[3] but it is now assigned to the

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* NRCC No. 10396.

[1] P. C. WAILES, *Rev. Pure Appl. Chem.* 6, 61 (1956).

[2] N. A. SORENSEN, in *Chemical Plant Taxonomy* (edited by T. SWAIN), Academic Press, London (1963).

[3] B. M. JOHRI and S. P. BHATNAGAR, *Proc. Natl Inst. Sci., India*, 26B (suppl.), 199–220 (1960).

[4] H. U. STAUFFER, *Mitt. Bot. Museum Univ. Zurich* 217, 387 (1961), and references cited therein.

tribe Anthoboleae.[3,5] In the present work, the seed oils of a number of additional species were examined to provide data for possible taxonomic use.

RESULTS AND DISCUSSION

The list of species and their oil content is given in Table 1. All had a substantial content of glyceride oil. The relatively high refractive indices indicate a high degree of unsaturation.

Spectroscopic examination of the oils gave the results shown in Table 2. All had strong u.v. absorption at 229–230 nm, characteristic of the conjugated *trans*-enyne group and attributed to ximenynic acid. This acid is known to occur in *Pyrularia*[12] and in some *Santalum* species.[9] It was isolated in the present work from *S. spicatum* and *S. yasi* and its presence was indicated in the other taxa by GLC.

Table 1. Seed oils of some santalaceae species

Species	Provenance	Oil content, % (air-dry basis)	n_D^{25}	Reference to previous work
Species examined for the first time:				
Buckleya lanceolata (Sieb. & Zucc.) Miquel	Kyoto, Japan*	37·2 a	1·4971	—
Geocaulon lividum (Richards.) Fern.	Slave River, N.W.T., Canada†	25·5 a	1·4840	—
Jodina rhombifolia Hook. & Arn.	Argentina†	31·9 a	1·4850	—
Santalum yasi Seem.	Fiji†	30·4 b	1·4889	—
Thesium humile Vahl	Italy*	—	—	—
Other species:				
Buckleya distichophylla Torr.	New York State, U.S.A.*	17·8 a	1·4941	6
Osyris alba L.	Belgium*	26·8 a	1·4826	7
Pyrularia pubera Michx.	Virginia, U.S.A.†	62·5 b	1·4769	8
Santalum acuminatum A.DC.	Australia†	52·6 b	1·4779	9
S. album L.	France (commercial)	35·0 a	1·4904	10
S. spicatum A.DC.	Australia†	52·5 b	1·4775	11

Key: * From botanic garden; † From natural habitat; oil content, a = Whole seed including pericarp, b = Kernel (seed less pericarp).

Buckleya lanceolata had additional u.v. maxima at 216, 240, 255, 269 and 284 nm, indicative of the presence of the conjugated *trans*-enediyne group.[13] In *B. distichophylla*, this absorption pattern was due to exocarpic acid (III)[6] and it may be assumed that *B. lanceolata* has the same acid. *Thesium humile* had similar but weak absorption.

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[5] H. U. Stauffer, *ibid.* **213**, 9 (1959).

[6] C. Y. Hopkins and M. J. Chisholm, *Chem. & Ind.* 1533 (1966).

[7] K. L. Mikolajczak, F. R. Earle and I. A. Wolff, *J. Am. Oil Chemists' Soc.* **40**, 342 (1963).

[8] C. Y. Hopkins, A. W. Jevans and M. J. Chisholm, *Chem. & Ind.* 998 (1967).

[9] H. A. Hatt and A. Z. Szumer, *Chem. & Ind.* 962 (1954).

[10] F. D. Gunstone and M. A. McGee, *Chem. & Ind.* 1112 (1954).

[11] H. A. Hatt and R. Schoenfeld, *J. Sci. Food Agric.* 7, 130 (1956).

[12] C. Y. Hopkins, A. W. Jevans and M. J. Chisholm, *J. Chem. Soc.*, in press.

[13] J. D. Bu'Lock and G. N. Smith, *Phytochem.* 2, 289 (1963).

TABLE 2. SPECTROSCOPIC EXAMINATION OF OILS AND METHYL ESTERS

Species	U.v. absorption of oils		Acetylenic acid as C-18 acid, %*	I.r. Absorption of methyl esters, ν_{max} cm^{-1}	
	$\lambda_{max, nm}$	$E(1\%\ 1\ cm)$		*ca.* 948	*ca.* 3600
Buckleya distichophylla	230	110	12X	M†	Tr
	269	211	29E		
B. lanceolata	230	94	9X	M	O
	269	299	40E		
Geocaulon lividum	229	209	37·5X	S	W
Jodina rhombifolia	230	308	55X	VS	M
Osyris alba	230	358	64X	VS	W
Pyrularia pubera	229	170	30·5X	VS	W
Santalum acuminatum	230	216	39X	VS	O
S. album	229	417	75X	VS	O
S. spicatum	230	191	34X	S	O
S. yasi	230	461	83X	VS	O
Thesium humile	229	236	42X	S	O
	268	33	4·5E		

* X, Calcd. as ximenynic acid after correcting for absorption due to exocarpic acid. E, Calcd. as exocarpic acid.

† Intensity recorded as none (O), trace (Tr), weak (W), medium (M), strong (S), or very strong (VS).

The i.r. spectra of the methyl esters, prepared from the oils, confirmed the presence of the enyne chromophore in all of the species listed (ν_{max} 948 cm^{-1}). A band at 3600–3610 cm^{-1} showed the presence of a hydroxy acid component in *Geocaulon*, *Jodina*, *Osyris*, and *Pyrularia*. In addition, *Jodina* and *Pyrularia* had maxima at 903 cm^{-1}, characteristic of a component with terminal vinyl unsaturation. An acid (V) of this class was isolated previously from *Pyrularia*.[12]

Hydrogenation of the total methyl esters, followed by GLC analysis, gave the relative proportions of C-16, C-17, and C-18 acids (unsubstituted). The C-16 content was unusually low, ranging from 1–4 per cent (cf. Ref. 7). Of the 11 species, only *Jodina* and *Pyrularia* had an appreciable amount of C-17 acid (16 and 6 per cent respectively).

The results are summarized in Table 3, along with information on other species reported by previous workers. Although there are many blank spaces (representing components which may or may not be absent), it is possible to make a tentative grouping of the various genera.

Aside from the ordinary acids such as palmitic and oleic, *Santalum* species have mainly ximenynic acid, with occasional small amounts of stearolic and hydroxy acids. Somewhat more unsaturation (dienyne) is evident in single species of three genera (Table 3). The enediyne group (e.g. exocarpic acid) appears in *Thesium*, *Buckleya*, and one species of *Exocarpus*. The remaining examples in Table 3 have a hydroxy acid, with more complex mixtures occurring in *Jodina*, *Pyrularia*, and *Acanthosyris*.

A tentative classification can thus be made on the basis of the acidic components, as follows:

Group 1. *Santalum* and some *Exocarpus* sp.; much ximenynic.

Group 2. *Omphacomeria*, *Leptomeria*, *Exocarpus*, (one species of each); ximenynic and dienynoic.

Group 3. *Thesium*, *Buckleya;* ximenynic and exocarpic.

Group 4. *Comandra*, *Osyris*, *Geocaulon;* ximenynic and some hydroxy acid.

Group 5. *Jodina*, *Pyrularia*, *Acanthosyris;* ximenynic, C-17, hydroxy, and terminal vinyl acids.

Table 3. Some fatty acid components of Santalaceae seed oils

		Identity or class of acid						
Species	Reference	Stearolic	Enyne as ximenynic	Dienyne	Enediyne as exocarpic	C-17	Hydroxy	Terminal vinyl
Santalum acuminatum	*9, 14, 15	+	+	0	0	0	0	0
S. album	*10, 14, 16	+	+			0	+	0
S. murrayanum	9	+						
S. spicatum	*11		+	0	0	0	0	0
S. yasi	*		+	0	0	0	0	0
Leptomeria aphylla	17		+	0	0			
Exocarpus cupressiformis	14, 18	+	+	0	0			
E. strictus	18		+	0	0			
E. nanus	19		+	+	0			
Omphacomeria acerba	19		+	+	0			
Leptomeria acida	19		+	+	+			
E. sparteus	19		+	0	+			
Thesium australe	19		+	0	+			
T. humile	*		+	0	+	0	0	0
Buckleya lanceolata	*		+	0	+	0	0	0
B. distichophylla	*6		+	Tr	+	0	0	0
Comandra pallida	7		+				+	
Osyris alba	*7		+	0	0	0	+	0
Geocaulon lividum	*		+	0	0	0	+	0
Jodina rhombifolia	*		+	0	0	+	+	Tr
Pyrularia pubera	12	+	+	0	0	+	+	+
Acanthosyris spinescens	20, 21		+	0	0	+	+	+

Key: * Present work; + Present; 0, Absent; Blank, Undetermined.

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[14] L. J. Morris and M. O. Marshall, *Chem. & Ind.* 460 (1966).

[15] F. D. Gunstone and R. Subbarao, *Chem. & Ind.* 461 (1966).

[16] F. D. Gunstone and A. J. Sealy, *J. Chem. Soc.* 5772–5778 (1963).

[17] H. H. Hatt, A. C. K. Triffett and P. C. Wailes, *Australian J. Chem.* **13**, 488 (1960).

[18] H. H. Hatt, A. C. K. Triffett and P. C. Wailes, *Australian J. Chem.* **12**, 190 (1959).

[19] H. H. Hatt, A. Meisters, A. C. K. Triffett and P. C. Wailes, *Australian J. Chem.* **20**, 2285 (1967).

[20] R. G. Powell and C. R. Smith, Jr., *Biochemistry* **5**, 625 (1966).

[21] R. G. Powell, C. R. Smith, Jr., C. A. Glass and I. A. Wolff, *J. Org. Chem.* **31**, 528 (1966).

All but two of the above genera were placed by Engler and Diels in the large tribe Osyrideae.[22] *Exocarpus* was classed in the tribe Anthoboleae and *Thesium* in the tribe Thesieae. The grouping shown above, based on fatty acid composition, suggests that subdivision of the tribe Osyrideae is warranted. Indeed, Johri and Bhatnagar[3] have done so, on the basis of embryological studies, although they did not examine all of the genera treated here.

Stauffer[5] transferred the genus *Omphacomeria* from Osyrideae to the tribe Anthoboleae and stated that it is closely allied to *Exocarpus*, on the basis of morphology. He also considered that *Pyrularia* might be placed in a special sub-family of Santalaceae,[23] along with *Scleropyrum* and other un-named genera. As shown above, the fatty acid components of *Pyrularia*, *Jodina*, and *Acanthosyris* are markedly different from those of other genera and thus there is chemical evidence for placing them in a separate tribe or sub-family. *Jodina* and *Acanthosyris* are similar in their morphological features.[4]

EXPERIMENTAL

Oils were extracted from the ground seeds with petrol. ether (b.p. 30–60°). U.v. spectra were determined in cyclohexane and i.r. spectra in CS_2. The content of two of the individual acids was calculated from the following values, determined with pure samples: ximenynic, E (1 per cent 1 cm) 557 at 229·5 nm; exocarpic, 738 at 269 nm. Methyl esters were prepared from oils or acids by heating with methanol-HCl. Hydrogenation was carried out in ether solution with Adams platinum catalyst. The liquid phase in GLC was a diethylene glycol-succinic acid polyester.

Buckleya lanceolata oil was similar to that of *B. distichophyla*[6] and had an apparent content of 40 per cent of exocarpic acid. After hydrogenation, the acids consisted of about 1 per cent palmitic and 99 per cent stearic acid (GLC).

Geocaulon lividum oil resembled the *Santalum* oils but had an appreciable content of hydroxy acid (ν_{max} 3610 cm^{-1}). It contained only 1 per cent of palmitic acid.

Jodina rhombifolia oil had no u.v. absorption above 230 nm, thus no greater unsaturation then enyne. It had fairly strong i.r. absorption at 3600 cm^{-1} (OH) and weak absorption at 903 ($CH_2{=}$). The content of palmitic acid was about 4 per cent of the total acids. After total hydrogenation, the non-hydroxy acids consisted of C-16, 5 per cent; C-17, 22 per cent; C-18, 73 per cent. The oil was similar to *Acanthosyris* oil[20,21] in its high content of C-17 acid and hydroxy acid.

Ximenynic acid was isolated from the oils of *Santalum yasi* and *S. spicatum* as follows. The oil was hydrolyzed and unsaponifiable matter was removed. The acids were crystallized from acetone (10 ml per g) at low temperatures. Saturated acids were removed at −10° and the main fraction was collected at −35°. It was crystallized twice from pentane (at −20° and −12°), yielding pure ximenynic acid, m.p. and mixed m.p. 38–39°. After hydrogenation of the total acids of *S. yasi*, GLC showed 1 per cent of palmitic acid but no C-17 acid. The oil contained a rubbery material, precipitated by acetone, as observed by Hatt in other *Santalum* oils.[11]

Thesium humile oil consisted mainly of octadecenoic and ximenynic acids, with a small amount of enediyne acid (GLC and u.v.). The u.v. maxima were at 229·5, 240 (infl.), 253 (infl.), 268, and 284 nm (enyne + enediyne). The i.r. spectrum showed no evidence of hydroxy (*ca.* 3600) or terminal vinyl groups (*ca.* 905 cm^{-1}).

Acknowledgements—We thank A. W. Jevans for most of the GLC data, R. Lauzon for infrared spectra, and J. A. Ogrodnik for other determinations.

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[22] A. Engler and L. Diels, *Syllabus der Pflanzenfamilien*, Gebrüder Borntraeger, Berlin (1936).

[23] H. U. Stauffer, private communication.