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DETERMINATION OF CYANOLIPIDS IN SEED OILS OF THE SAPINDACEAE BY MEANS OF THEIR NMR SPECTRA

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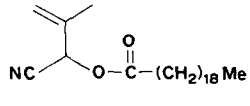
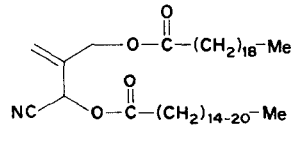
Key Word Index—*Paullinia tomentosa*; *Sapindus utilis*; *S. drummondii*; *Ungnadia speciosa*; *Koelreuteria paniculata*; *Cardiospermum hirsutum*; Sapindaceae; fatty acid esters; 1-cyano-2-hydroxy-methylprop-2-ene-1-ol; 1-cyano-2-methylprop-1-ene-3-ol; 1-cyano-2-methylprop-2-ene-1-ol; 1-cyano-2-methylprop-1-ene-3-ol; NMR.

Abstract—Analysis of the NMR spectra has been developed as a method for the measurement of the type and amount of cyanolipids in seed oils. The cyanolipids of 6 species of Sapindaceae are reported.

TO DATE cyanolipids have been isolated only from seed oils of the family Sapindaceae, with one anomalous exception *Cordia verbenacea*, a borage. These compounds are somewhat unstable, especially upon hydrolysis, but may be isolated by column chromatography and preparative TLC.[1] Both of these procedures are time consuming; therefore we have developed the use of NMR spectra of the chloroform extracted seed oils to determine the presence and amount of cyanolipids and the glycerides with which they occur. All four known cyanolipids (**1**–**4**) may be distinguished from each other and from glycerides by this method.



(1)



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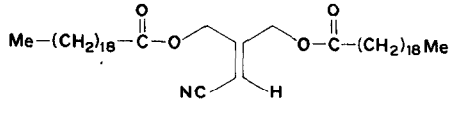

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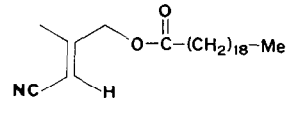

(4)

In most seed oils examined, one cyanolipid is predominant, except that compounds **3** and **4** occur together in several seed oils as major components.[2] By comparison of the integrals associated with diagnostic NMR peaks, it is possible to obtain relative percentage values for cyanolipids and glycerides.

[1] MIKOLAJCZAK, K. L., SMITH, JR., C. R., and TJARKS, L. W. (1970) *Lipids* **5**, 812.
[2] MIKOLAJCZAK, K. L., SMITH, JR., C. R., and TJARKS, L. W. (1970) *Lipids* **5**, 672.

A summary of the NMR peaks which may be used to determine the amount of the cyanolipids is given below in Table 1.

TABLE 1. SUMMARY OF THE NMR PEAKS USED TO DIFFERENTIATE CYANOLIPIDS*

Component	Methyl	Vinyl	AB	–O– –CH–	CH_2–O–*	C NC H O– cyanohydrin
Glycerides	—	Triplet cent. at 5·4 in fatty acids	—	5·4	Pair of Quartets cent. at 4·12	—
1	1·97	5·17 5·3*	—	—	—	5·79
2	—	5·61 5·4*	4·58	—	—	5·88
3	—	5·2*	4·88 4·68	—	—	—
4	1·96	5·2*	4·73	—	—	—

All chemical shifts are reported in delta values relative to TMS.
* Indicates the peak overlaps fatty acid vinyl absorptions.

Vinyl absorptions which overlap fatty acid vinyl absorptions are still qualitatively useful and in cyanolipid-glyceride mixtures with low unsaturation may also be used quantitatively. The presence of compounds **3** and **4** is also indicated by the presence of a nitrile band (2230 cm^{-1}) in the IR spectrum, whereas no corresponding band exists in the spectra of **1** and **2**.[1-3]

By use of this method we have determined the cyanolipid content of numerous seed oils, several of which are reported in Table 2.

TABLE 2. RELATIVE PERCENTAGES OF CYANOLIPIDS (**1**–**4**) AND GLYCERIDES FROM SAPINDACEOUS SEED OILS

Species	Glycerides	**1**	**2**	**3**	**4**
** *Sapindus utilis**	68	—	—	32	—
** *S. drummondii*†	72	—	—	28	—
** *Paullinia tomentosa*‡	74	—	26	—	—
Koelreuteria paniculata§	44	—	—	25	31
Ungnadia speciosa‖	67	33	—	—	—
** *Cardiospermum hirsutum*¶	50	—	50	—	—

* Seed specimen from Plant Introduction Station, U.S.D.A., Chico, California.
† DS-972, 5 miles east of Hext, Texas, Mason Co.
‡ Ventura 7990. Seed specimen provided by Dr. J. Rzedowski, Instituto Politecnico Nacional, México, México.
§ DS-6219, University of California Campus, Davis, California.
‖ Seed specimen from Pedernales River and State Highway 71, Travis Co. Texas.
¶ DS-1022, Goleta, California, Santa Barbara Co.
** Previously unreported.

We were unable to detect cyanolipids in *Xanthoceras sorbifolia*, *Dodonea visosa*, *Paullinia cupana*, *Litchi chinensis*, *Euphoria longana*, *Blighia sapida*, or *Staphylea trifolia*

[3] SEIGLER, D. S., MIKOLAJCZAK, K. L., SMITH, JR., C. R., WOLFF, I. A. and BATES, R. B. (1970) *Chem. Phys. Lipids* **4**, 147.

(Staphyleaceae) seed oils. The seed meal of *Paullinia cupana* was, however, strongly cyanogenic.

EXPERIMENTAL

All seed oils were isolated by $CHCl_3$ extraction of seed meals prepared by grinding with a Waring Blender. The extracts were concentrated under vacuum and refrigerated until spectral measurement was possible. NMR spectra were measured with a 100mhz Varian instrument in $CDCl_3$ using TMS as an internal standard. IR spectra were measured on a Beckman IR-33 instrument as smears.

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