Phytochemistry, 1971, Vol. 10, pp. 485 to 487. Pergamon Press. Printed in England.

SAPINDACEAE

NEW CYANOGENETIC LIPIDS FROM *UNGNADIA SPECIOSA*

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(*Received* 10 *June* 1970)

Abstract—A mixture of two new cyanogenetic lipids from the seeds of *Ungnadia speciosa* have been structurally characterized.

WE WISH to report the structure determination of a mixture of two new cyanogenetic lipids which are based upon the same aglycone but differ in the degree of saturation of their C_{20} lipid moieties (I). The mixture was obtained from the seed oil of a small tree, *Ungnadia speciosa*, which is indigenous to the southwestern United States and northern Mexico. Although several cyanogenetic lipids are known to occur in nature,[1-5] the detailed structure has been reported[1,2] for only one other mixture (II).

A pentane extract obtained from the seeds of *Ungnadia speciosa* afforded after chromatography* a mixture of two† cyanogenetic lipids to which we assign formula I based on the evidence presented below. Because the mixture was difficult to separate and appeared to be based on a single aglycone, it was treated as a single entity during the course of this investigation.

Although the new cyanogenetic lipid material readily liberated HCN by a standard picrate test,[1,2,6] the i.r. spectrum for the material did not display a band for nitrile absorption; however, this latter result is in accord with the available i.r. data for similar substances. The i.r. spectrum did exhibit bands at 1010 and 927 cm^{-1} which are typical for a terminal methylene group in the aglycone moiety of a cyanogenetic lipid.[1,2] The NMR spectrum of the material was particularly informative with regard to the structural features of the aglycone moiety: the cyanohydrin proton (H_2) appeared as a slightly broadened singlet at 5·79 δ, the C_5-vinyl methyl gave a finely split singlet at 1·89 δ and the two C_4-terminal methylene protons gave two finely split singlets at 5·17 and 5·33 δ. Spin decoupling experiments established that the small coupling observed for the C_5-vinyl methyl group resulted

* The cyanogenetic compounds from *Ungnadia speciosa*, unlike those of *Cordia verbenacea*,[1,2] were readily separated from various glycerides by silica gel chromatography. The glycerides obtained in the present investigation afforded upon trans-esterification and GLC analysis, the following relative amounts of fatty acid methyl esters: C_{16} (6·2%), C_{18}-unsaturated (66·0%), C_{18}-saturated (3·6%) and C_{20}-saturated (trace).

† Traces of other cyanogenetic lipids were probably present based upon the occurrence of minor peaks in the GLC of the methyl esters of the fatty acids obtained from the cyanogenetic lipid material.

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[2] D. S. SEIGLER, K. L. MIKOLAJCZAK, C. R. SMITH, JR., I. A. WOLFF and R. B. BATES, *Chem. Phy. Lipid* **4**, 147 (1970).
[3] L. ROSENTHALER, *Schweiz. Apoth.* **58**, 17 (1920); *Chem. Abs.* **14**, 556 (1920).
[4] M. K. KUNDU and C. BANDYOPADHYAY, *J. Am. Oil Chem. Soc.* **46**, 23 (1969).
[5] M. G. KASBEKER and N. V. BRINGI, *J. Am. Oil Chemists' Soc.* **46**, 183 (1969).
[6] T. WOOD, *J. Sci. Food Agri.* **16**, 300 (1965).

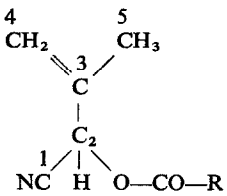
from interaction with the terminal methylene protons and the cyanohydrin proton. Coupling was also detected between the latter proton and the methylene group.

When the mixture was hydrogenated,* material was obtained which appeared to be a single substance and whose NMR spectrum exhibited a doublet ($J = 5{\cdot}6$ c/s) at 5·18 δ for the cyanohydrin proton and two overlapping doublets ($J = 6{\cdot}0$ c/s) at 1·22 δ for the C_4 and C_5 methyl groups. The i.r. spectrum for the hydrogenated material did not exhibit bands for a terminal methylene group. These spectral findings for the material before and after hydrogenation indicated that the structure of the aglycone moiety of the mixture of new cyanogenetic lipids must be 1-cyano-2-methylprop-2-ene-1-ol as shown in I.†

The only remaining question concerned the nature of the two lipid groups. The NMR spectrum of the original cyanogenetic lipid material exhibited a number of signals characteristic for long-chain lipid groups: the α-protons of the fatty acids gave rise to a triplet (J 7·2 c/s) at 2·39 δ (unchanged in the hydrogenated material) a distorted triplet appeared at 0·88 δ for the terminal methyl groups, the vinyl protons appeared as a triplet centered at 5·36 δ ($J = 4{\cdot}6$ c/s) and a large broad signal for the methylene protons was centered at 1·25 δ. The lipid groups were identified by converting them to their methyl esters by transesterification and comparing the methyl esters by GLC with authentic standards. Thus, the lipid groups were found to consist of 71·6 per cent of a C_{20} mono-unsaturated fatty acid group and 28·4 per cent of the C_{20} saturated fatty acid moiety.

Finally, the mass spectrum of the original mixture of cyanogenetic lipids showed parent ions at *m/e* 389 and 391 whereas the mass spectrum of the hydrogenated material showed only a single parent peak at 393.

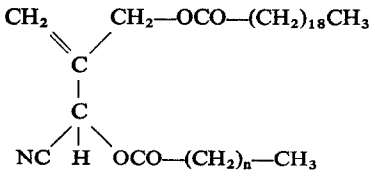
Based on all the above data, structure I is assigned to the two cyanogenetic lipids from *Ungnadia speciosa:*



R = $(CH_2)_{18}\,CH_3$
R = C_{19} with one double bond (probably $\Delta^{9,10}$)

I

they are, therefore, similar to the cyanogenetic lipids (II) from *Cordia verbenacea.*



n = 14, 16, 18, 20 (corresponding mono-unsaturated acids also occur).

II

* Hydrogenation of cyanogenetic lipids is generally accompanied by some hydrogenolysis. However, the hydrogenolysis can be minimized by maintaining low temperatures, using Pd-C as catalyst and by working up the reaction mixture as soon as rapid uptake of hydrogen has ceased.

† The aglycone has not yet been isolated by hydrolysis of the cyanogenetic lipids; only decomposed material has been obtained from a number of attempts.

EXPERIMENTAL

I.r. spectra were determined in CCl_4; NMR spectra were recorded with a Varian HA-100 spectrometer in $CDCl_3$. The spin decoupling experiments were performed by adding some C_6D_6 to the $CDCl_3$ solutions. All chemical shifts are reported in ppm (δ) relative to internal TMS. The mass spectra were measured with a Bell & Howell 21-491 mass spectrometer. The sample was inserted with a probe, and 70 e.v. ionization was used. The methyl esters obtained from the lipid moieties of the glycerides and the cyanogenetic materials were prepared by trans-esterification and characterized by GLC comparison with known standards; the GLC analyses were determined on a Varian 1520C gas chromatograph fitted with 10 ft × 0·125 in. stainless steel columns, packed with either 5% SE-30 (130°–250°, 1°/min) or 5% Carbowax 20 M (isothermal, 200°) liquid phases.

Isolation of the cyanogenetic lipids. Seeds (132 g) of *Ungnadia speciosa* (collected near the Pedernales River, on State 71, west of Austin, Texas) were ground in a Waring Blendor and extracted with *n*-pentane overnight. The pentane was removed to yield a light yellow oil (41·5 g; 31·4%). The crude oil (3·0 g) was placed on a column of silica gel (200 g) packed in hexane and eluted with hexane containing increasing amounts of ether. The cyanogenetic lipids were eluted with 2% ether in hexane. Evaporation of the solvent gave a colorless oil (0·44 g). This oil gave a strongly positive test for HCN with the picrate test.[6] The lipid materials had $[\alpha]_D^{25} = +9{\cdot}28°$ (c = 1·4, hexane) and showed a plain positive ORD curve.

The cyanogenetic lipids were chromatographed on silica gel G plates with a mixture of hexane–ether–HOAc (95:5:1). The plates were sprayed with 0·2% solution of 2′,7′-dichlorofluoroscein in ethanol and viewed in u.v. light.

Hydrogenation of the cyanogenetic lipids. The cyanogenetic lipids (0·097 g) were added to hexane containing 5% Pd-C which had been previously reduced at room temperature and atmospheric pressure. After stirring the reaction mixture for about 5 min the hydrogen uptake slowed, and the catalyst was removed by filtration. After removal of the hexane, a white solid (0·091 g, 94% yield) was obtained. The hydrogenated material had $[\alpha]_D^{25} = +27{\cdot}9°$ (c = 0·43, hexane) and showed a plain positive ORD curve.

Acknowledgements—We thank the Robert A. Welch Foundation (Grant F-130), the National Science Foundation (Grant GB-5548X), and the National Institutes of Health (Grant HD 04488) for financial support. The senior author was the recipient of a University of Texas post-doctoral fellowship, 1968-1970.

Phytochemistry, 1971, Vol. 10, pp. 487 to 490. Pergamon Press. Printed in England.

MONOCOTYLEDONAE

GRAMINAE

BETA-DIKETONE, ALCOHOL AND HYDROCARBONS OF BARLEY SURFACE LIPIDS

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(*Received* 8 *April* 1970)

Abstract—Glaucous lines of barley have the β-diketone, hentriacontan-14,16-dione, in their surface lipids. The aliphatic alcohol of barley surface lipid is 1-hexacosanol, and the principal hydrocarbons have carbon numbers 25, 27, 29, 31 and 33. There is no apparent biosynthetic relationship between the primary alcohol and the β-diketone; however, there may be some relationship between the β-diketone and the hydrocarbons.

INTRODUCTION

THIS study was prompted by the observation that during mid-summer 'wild type' barley had a glaucous 'bloom' and mutants of these lines were non-glaucous. Examination of the