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DEIDACLIN FROM *TURNERA ULMIFOLIA*

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Key Word Index—*Turnera ulmifolia*: Tuneraceae; cyanogenic glycoside; deidaclin.

Turnera ulmifolia L. is a shrubby perennial, tropical American plant that has been reported cyanogenic by [1]. The Turneraceae has long been considered to be closely related to the Passifloraceae and Flacourtiaceae [2, 3]. Members of the latter two families are unique in producing cyclopentenoid cyanogens. Gynocardin has been isolated from the Flacourtiaceae [4], and gynocardin, tetraphyllin A, tetraphyllin B (barterin), *epi*-tetraphyllin B and deidaclin have been isolated from the Passifloraceae [1, 5–8]. In reporting the isolation of deidaclin from *Turnera ulmifolia*, we offer further evidence of the affinity of the Turneraceae with the Passifloraceae and Flacourtiaceae. This is only the second report of deidaclin from a natural source.

The NMR spectrum of the TMS ether of the unknown (Fig. 1) proved to be identical with that of the TMS ether of deidaclin previously reported [9]. The presence of a single glucose unit as the sugar moiety of the cyanogen was confirmed by the glucose oxidase method. The field-desorption MS (source temperature 100°) of the unknown showed strong peaks at *m/e* 272 (M + 1), 245 (M − 26), 163 and 164 and a doublet at *m/e* 92 and 93. These data are consistent with those of refs. [8] and [9].

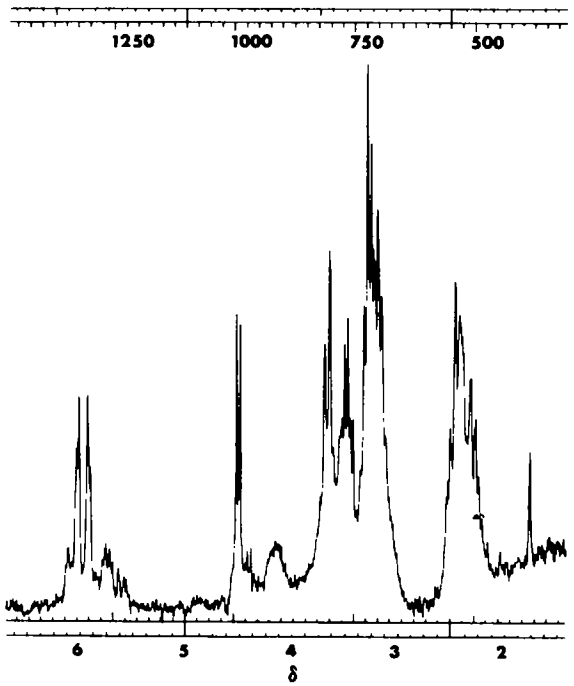

Fig. 1. NMR spectrum of the TMS ether of deidaclin.

EXPERIMENTAL

Isolation and purification of the glycoside. Leaves and stems of *Turnera ulmifolia* (80 g) were added to boiling 80% MeOH. The resulting suspension was filtered and the residue washed with 80% MeOH (500 ml). The extract was concd to yield a brown syrup (20 ml). This was extracted with $CHCl_3$, the aq. phase retained and placed on a Sephadex column (G-10). Fractions were collected (50 × 5 ml) with H_2O as eluant. A few drops of each fraction were transferred to a vial, buffered to pH 6.8 and a few drops of enzyme prepn added (see below). HCN released as a result of enzymatic hydrolysis was detected with Feigl–Anger paper [10]. The cyanogenic material (fractions 11–22) was concd to *ca* 5 ml and chromatographed on paper (Whatman 3MM, 22 × 57) in MeCOEt–Me_2CO–H_2O (15:5:3). The cyanogen was detected by cutting a strip 1 cm wide from the center of the chromatogram, cutting 1 cm^2 sections from this strip, placing them in vials and testing for HCN as above. The cyanogen (R_f 0.45) was eluted with H_2O, concd *in vacuo* and rechromatographed on paper in Me_2CO–H_2O (5:1). The cyanogen (R_f 0.74) was eluted, concd *in vacuo* and chromatographed a final time in MeCOEt–Me_2CO–H_2O (15:5:3). The purified cyanogen was eluted and concd as above to yield a viscous yellow solid (66.5 mg, overall yield was 0.83%).

Enzyme preparation. Leaves of *Passiflora foetida* L. (100 g) were ground in a blender with 500 ml Me_2CO. The suspension was then filtered and rinsed with Me_2CO (250 ml). Solid material retained in the filter was dried *in vacuo*, resuspended in pH 6.8 Pi buffer (500 ml), stirred in an ice bath for 1 hr and then filtered. The filtrate was dialysed against pH 6.8 buffer for 12 hr. The product was concd *in vacuo* to a final vol. of 50 ml and its hydrolytic activity confirmed by testing fresh leaves of *Turnera* by the Feigl–Anger method.

Determination of sugar. Quantitative determination of glucose was made using the glucose oxidase method [11]. The cyanogen was incubated with the above enzyme prepn for 4 hr, then subjected to the glucose oxidase test. The results indicate the presence of 1 mol glucose per mol cyanogen (0.5 mg deidaclin = 1.8 mol, observed glucose activity = 1.8 mol).

Spectral determinations. The NMR spectrum was measured on a Varian HA-220 spectrometer as the TMS derivative in $CDCl_3$. These derivatives were prepared as previously described [9]. The MS was measured on a Varian 311A spectrometer (low resolution, field desorption).

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REFERENCES

1. Tantisewie, B., Ruijgrok, H. W. L. and Hegnauer, R. (1969) *Pharm. Weekbl.* **104**, 1341.
2. Cronquist, A. (1968) *The Evolution and Classification of Flowering Plants.* Houghton Mifflin, Boston.
3. Thorne, R. F. (1976) A phylogenetic classification of the Angiospermae, in *Evolutionary Biology*, Vol. 9. Plenum Press, New York.
4. Coburn, R. A. and Long, L. (1966) *J. Org. Chem.* **31**, 4312.
5. Russell, G. B. and Reay, P. F. (1971) *Phytochemistry* **10**, 1373.
6. Paris, M., Bouquet, A. and Paris, A. (1969) *C.R. Acad. Sci.* **268**, 2804.
7. Gondwe, A. T. D., Seigler, D. S. and Dunn, J. E. (1978) *Phytochemistry* **17**, 271.
8. Clapp, R. C., Ettlinger, M. G. and Long, L., Jr. (1970) *J. Am. Chem. Soc.* **92**, 6378.
9. Seigler, D. S. (1975) *Phytochemistry* **14**, 9.
10. Feigl, F. and Anger, V. A. (1966) *Analyst* **91**, 282.
11. Washko, M. E. and Rice, Z. W. (1971) *Clin. Chem.* **7**, 542.

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A NEW ACETYLENIC ALCOHOL FROM *CIRSIUM JAPONICUM*

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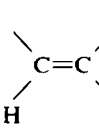
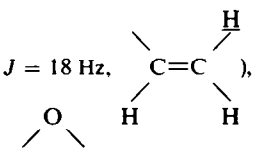
Key Word Index—*Cirsium japonicum*; Compositae; root oil; *cis*-8,9-epoxy-heptadeca-1-en-11,13-diyn-10-ol.

Dihydro- and tetrahydro-aplotaxene of the root oil from *Cirsium japonicum* have been the subject of previous studies [1]. From the polar component of the root oil a new acetylene alcohol **1** was isolated and purified using column chromatography and TLC.

MS of **1** showed a M^+ at *m/e* 260. On hydrogenation, **1** consumed 5 molar equivalents of hydrogen and gave decahydroalcohol **4**, mp 63–64°, $C_{17}H_{34}O_2$. **1** thus is $C_{17}H_{24}O_2$. IR of **1** showed the presence of a hydroxyl (3400 cm^{-1}), an acetylene (2255 cm^{-1}) and a vinyl group (3080, 1640, 995, 910 cm^{-1}). Epoxide absorption was observed at 835 cm^{-1} corresponding to a *cis*-conformation. ^1H NMR provided additional information about the structure of **1**; a hydroxyl group at 2.59 ppm (1 H, *s*, OH, disappeared with D_2O), a vinyl group at 5.81 (1 H, *m*, $CH{=}CH_2$), 4.95 (1 H, *d–m*, J = 9 Hz, ), 5.0 (1 H, *d–m*, J = 18 Hz, ), an epoxide group at 3.0 (2 H, *m*, $CH{-}CH$), a $-CH_2-$ group connected to a double bond at 2.05 (2 H, *m*, $CH_2{-}C{=}C$), a Me group at 1.02 (3 H, *t*, J = 7 Hz, $CH_3{-}CH_2$), a secondary alcohol group situated between the acetylene and an epoxide at 4.26 (1 H, *d*, J = 7 Hz, $C{\equiv}C{-}CH[OH]{-}CH{-}CH$), and a $-CH_2-$ group situated between a $-CH_2-$ and the acetylene at 2.28 (2 H, *t*, J = 7 Hz, $CH_2{-}CH_2{-}C{\equiv}C$). By comparing the ^1H NMR spectra of **1** and two C_{17}-acetylenes (**2** [2] and **3** [3]) isolated from *Erodiophyllum elderi* and *Anthemis rudolfiana*, **1** has three partial structures of $Me{-}CH_2{-}CH_2{-}C{\equiv}C$, $C{\equiv}C{-}CH(OH){-}CH{-}CH$ and $CH_2{-}CH{=}CH_2$. When the $-CH_2-$ protons at 1.57 ppm situated between a Me and $CH_2{-}C{\equiv}C$ group had been decoupled, a Me group at 1.02 ppm changed from the typical triplet to a singlet and also a $-CH_2-$ group at 2.28 ppm connected to the acetylene group changed from a triplet to a singlet signal. In the same manner, a doublet proton at 4.26 ppm of a secondary alcohol group was decoupled, and the multiplet signal of the epoxide proton changed to the doublet signal with a coupling constant of 3.5 Hz corresponding to a *cis*-conformation. The coupling constant of *cis*-epoxides is usually 3 Hz [4, 5], whilst that of *trans*-epoxides is *ca* 2 Hz [6, 7]. MS of **1** shows peaks at *m/e* 91 (49%, n-C_3H_7-$[C{\equiv}C]_2$), 121 (100, n-$C_3H_7{-}[C{\equiv}C]_2{-}CH[OH]$) and 163 (16, n-$C_3H_7{-}[C{\equiv}C]_2{-}CH[OH]{-}CH{-}CH$), and supports the structure of **1** [2]. **4** after hydrolysis with 2 N H_2SO_4 gave a triol, which was converted into two molecules of capryl aldehyde after treating with $NaIO_4$ [3].