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APLOTAXENE EPOXIDE FROM *CIRSIUM HYPOLEUCUM*

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Key Word Index—*Cirsium hypoleucum*, *C. canum*, *C. carolinianum*; Compositae; aplotaxene epoxide; 11,12-epoxyheptadeca-1,8,14-triene; lupeol; taraxasterol; β-amyrin.

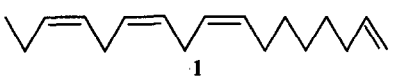
Abstract—Aplotaxene epoxide (11,12-epoxyheptadeca-1,8,14-triene) was isolated from the roots of *Cirsium hypoleucum*. The pentacyclic tritepenes lupeol, taraxasterol and β-amyrin, and other acetates, were identified in *C. hypoleucum*, *C. canum* and *C. carolinianum*.

So far from *Cirsium* species (Compositae, tribe Cynareae) no characteristic compounds have been isolated but they contain numerous flavones [1], triterpenes (ref. [2] and lit. within) and some widespread polyacetylenes [3]. From two species several unsaturated C_{17}-hydrocarbons have been reported [4]. We have now investigated two species from Turkey, *C. hypoleucum* DC and *C. canum* (L.) All. The roots of the first species contained aplotaxene (**1**), the pentaynene **3** [3], the enetetraynene **4** [3] and the rare furanosesquiterpene **5** with unknown stereochemistry, isolated before from a *Vernonia* species [5]. Furthermore, the epoxide **2** was present and its structure followed from the ^{1}H NMR spectral data, especially when compared with those of **1**. The position of the epoxide group was deduced from the absence of the downfield methylene signals (10- and 13-H) and the presence of a symmetrical signal for the epoxide protons (Table 1). Although the stereochemisty of the epoxide could not be determined *cis* configuration is likely based upon biogenetic considerations.

Table 1. ^{1}H NMR spectral data of compound **2** (270 MHz, C_6D_6, TMS as internal standard)

1-H	5.07 *ddt*
1′-H	5.02 *ddt*
2-H	5.82 *ddt*
3-, 7-, 16-H	2.00 *m*
4-, 6-H	1.35 *m*
8-, 9-, 14-, 15-H	5.5 *m*
11-H, 12-H	2.83 *m**
10-H	2.40 *m*
13-H	2.18 *m*
17-H	0.93 *t*

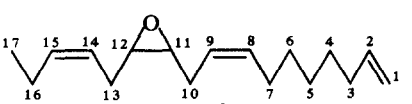
* Symmetrical ten-line signal (J = 4 and 2).
J (Hz): 1, 1′ = 1, 3 = 1.5; 1, 2 = 17; 1′, 2 = 10; 2, 3 = 7; 16, 17 = 7.5.



1

Me[C≡C]$_5$CH=CH$_2$

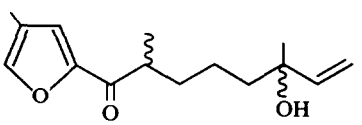
3



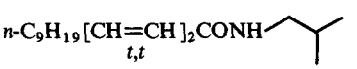
2

MeCH=CH[C≡C]$_4$CH=CH$_2$

4



5



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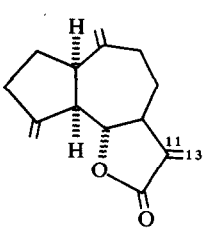
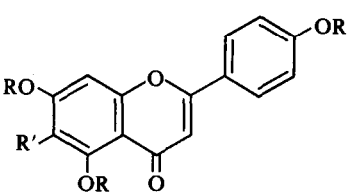


7 **8** = 11, 13-H



9 R = R′ = H
10 R = H, R′ = OMe
11 R = Ac, R′ = OMe

The aerial parts afforded **1**, **5**, lupeol, lupeyl acetate, squalene, β-amyrin, β-amyrin acetate and taraxasterol acetate. The roots of *C. canum* also contained **1**, **4**, lupeol, lupeyl acetate, taraxasterol, taraxasteryl acetate and the amide **6**, so far only isolated from species of the tribe Anthemideae [6]. The aerial parts afforded also **1**, **4**, lupeol, lupeyl acetate, taraxasterol and taraxasteryl acetate. The roots of the third species, *C. carolinianum* (Walt.) Fern. et Schub., collected in Louisiana, afforded lupeyl acetate and taraxasteryl acetate as well as the guaianolides **7** [7] and **8** [7], while the aerial part yielded again lupeyl acetate and taraxasteryl acetate as well as β-amyrin acetate and the flavones **9** and **10** [8]. The structure of **10** was established by transformation to the corresponding triacetate **11**. Comparing the ^{1}H NMR spectral data of **10** and **11** and the observed Eu(fod)$_3$ induced shifts allowed the assignment of the substitution pattern of the aromatic ring. This species was placed also in the genus *Carduus*. The lactones isolated may be an indication of this placement.

The results show again that no particularly characteristic compounds can be isolated from *Cirsium* species. Further investigations may show whether compounds like **5** may be of chemotaxonomic importance.

EXPERIMENTAL

The air-dried plant material was extracted with Et_2O–petrol (1:2) and the resulting extracts first separated by CC on Si gel and further by repeated TLC on Si gel. Known compounds were identified by comparing their IR and ^{1}H NMR spectra with those of authentic samples.

Cirsium hypocephalum (*voucher* 01237). The roots (200 g) afforded 30 mg **1**, 20 mg **2** (Et_2O–petrol, 1:20), 0.5 mg **3**, 0.5 mg **4** and 5 mg **5**, while the aerial parts (300 g) gave 5 mg **1**, 3 mg **5**, 40 mg lupeol, 10 mg lupeyl acetate, 40 mg β-amyrin, 10 mg β-amyrin acetate, 5 mg taraxasteryl acetate and 3 mg squalene.

Cirsium canum (*voucher* 01308). The roots (300 g) afforded 25 mg **1**, 2 mg **4**, 7 mg **6**, 10 mg lupeol, 10 mg lupeyl acetate, 5 mg taraxasterol and 6 mg taraxasteryl acetate, while the aerial parts yielded 20 mg **1**, 0.5 mg **4**, 16 mg lupeol, 10 mg lupeyl acetate, 4 mg taraxasterol and 10 mg taraxasteryl acetate.

Cirsium carolinianum (*voucher LV* 78/6). The roots (60 g) afforded 15 mg lupeyl acetate, 15 mg taraxasteryl acetate, 3 mg **7** and 12 mg **8**, while the aerial parts (500 g) yielded 20 mg lupeyl acetate, 20 mg taraxasteryl acetate, 20 mg β-amyrin acetate, 15 mg **9** and 10 mg **10**.

11,12-*Epoxyheptadeca*-1,8,14-*triene* (**2**), Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1640 (CH=CH), 990, 910 (CH=CH); MS (CI, isobutane) *m/e* (rel. int.): 249 ($M^+ + 1$, 100), 231 (249 − H_2O, 73), $[\alpha]_D$ + 13 (*c* = 0.87, $CHCl_3$).

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