Chemistry, the University of Illinois for the determination of NMR and MS.

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A NEW ACETYLENIC ALCOHOL FROM *CIRSIUM JAPONICUM*

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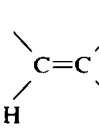
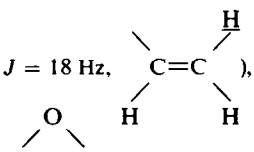
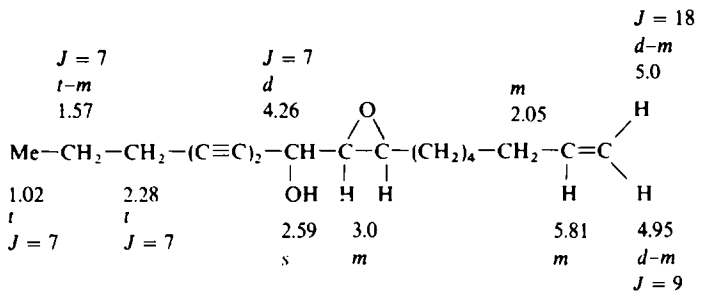
Key Word Index—*Cirsium japonicum*; Compositae; root oil; *cis*-8,9-epoxy-heptadeca-1-en-11,13-diyn-10-ol.

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].



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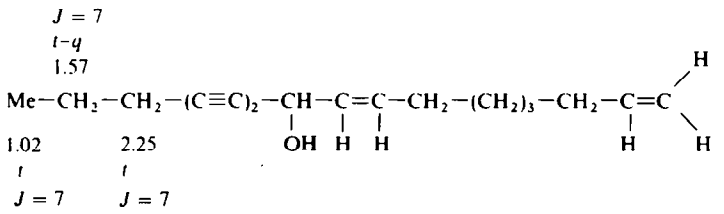

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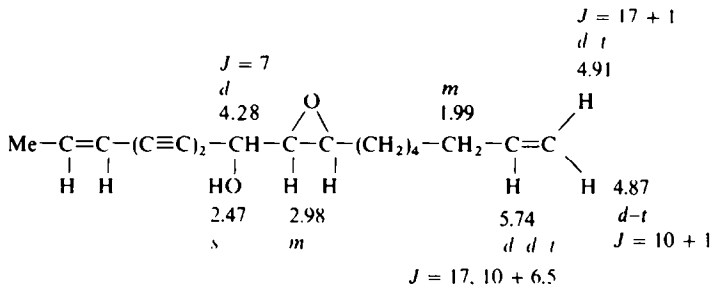

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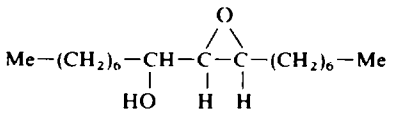

4

From the chemical and physical data, the structure of **1** was found to be *cis*-8,9-epoxy-heptadeca-1-en-11,13-diyn-10-ol.

EXPERIMENTAL

IR spectra were recorded as liquid films and in nujol. ^{1}H NMR spectra were determined using TMS as int. standard in CCl_4. GLC was carried out using 5% SE-30 (He 20 ml/min, 100°). The extract which was that described in our previous paper [1] was chromatographed on a deactivated Al_2O_3, and gave polar components (18% of extract).

cis-8,9-*Epoxy-heptadeca*-1-*en*-11,13-*diyn*-10-*ol* (**1**). The polar component (7.7 g) was rechromatographed on a Si gel column with hexane–EtOAc (4:1). A crude **1** (3.9 g) was isolated from the middle fraction. The fraction was purified by prep.-TLC with hexane–EtOAc (17:3) (R_f 0.29). MS (70 eV) showed peaks at *m/e* 41 (73%), 55 (70), 67 (48), 91 (49), 121 (100), 163 (16) and 260 (2). IR cm^{-1}: 3400, 3080, 2255, 1640, 1305, 1280, 1231, 1025, 995 and 835.

cis-8,9-*Epoxy-heptadecan*-10-*ol* (**4**). **1** (110 mg) was hydrogenated over Adams PtO_2 (25 mg) in HOAc and absorbed 5.2 mol of H_2. **4** was obtained, mp 63–64° from CCl_4. Found: C, 75.47; H, 12.58. Calc. for $C_{17}H_{34}O_2$: C, 75.50; H, 12.67%. IR 3520, 1310, 1286, 1260, 1062, 841 and 726 cm^{-1}. ^{1}H NMR showed signals at 0.88 ppm (6 H, *t*, *J* = 6 Hz, $[CH_3-CH_2]_2$), 1.89 (1 H, *s*, OH, disappeared with D_2O), 2.75 (2 H, *m*,  and 3.4 (1 H, *m*,

CH—OH). **4** (10 mg) dissolved in *p*-dioxane (3 ml) was warmed with 2 N H_2SO_4 (0.6 ml) for 15 min at 60°, and treated with $NaIO_4$ (50 mg) in 2 N H_2SO_4 (0.5 ml). After 10 min, the reaction mixture was extracted with Et_2O (50 ml). The Et_2O layer was washed with H_2O and reduced in vol. The reaction product was identified as capryl aldehyde (R_t = 5.1 min) by comparison with an authentic sample using GLC [3].

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ILEX-LACTON, EIN BISNORMONOTERPEN NEUARTIGER STRUKTUR AUS *ILEX AQUIFOLIUM**

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Key Word Index—*Ilex aquifolium*; Aquifoliaceae; Ilex lactone; bisnormonoterpene.

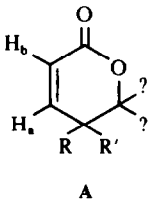
Abstract—The structure of Ilex lactone from *Ilex aquifolium* has been determined as 3-(3′-hydroxycyclopent-1-enyl)-*Z*-propenic acid-1,5′-lactone.

Aus den Früchten von *Ilex aquifolium* ließ sich ein Bisnormonoterpen (**1**) isolieren, für das wir den Namen Ilex-Lacton vorschlagen. Über die Strukturaufklärung wird im folgenden berichtet.

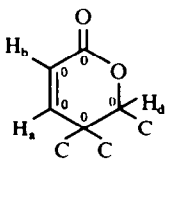
Massenspektroskopisch konnte die Summenformel als $C_8H_8O_3$ bestimmt werden. Das Fragmentierungsmuster selbst ist uncharakteristisch (s. Experimentelles). Im IR-Spektrum finden sich Banden bei 1725 und 1640 cm^{-1}, die von einem α,β-ungesättigten δ-Lacton herrühren können. Die wichtigsten Strukturinformationen stammen aus dem ^{1}H-NMR-Spektrum (s. Tabelle 1): Das 2-Protonen-AB-System (H_a und H_b) bestehend aus einem Doppeldublett und einem Doppeltriplett kann einer mit einer Carbonylgruppe konjugierten (nach der Größe der Kopplungskonstanten *Z*-) Doppelbindung zugeordnet werden, deren H-Signale nur durch Fernkopplung weiter aufgespalten sind. In Verbindung mit den IR-Daten ergibt sich daraus die Partialstruktur **A**.

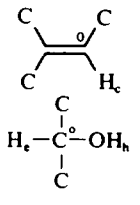
Damit sind zwei O-Atome festgelegt. Bei dem dritten handelt es sich um eine OH-Gruppe, da das Signal von H_h bei Zusatz von D_2O verschwindet.

H_d und H_e müssen—nach ihrer chemischen Verschiebung zu schließen—an C-Atome gebunden sein, die



A





B

O-substituiert sind, und zwar an zwei verschiedene C-Atome, da die beiden Protonen nicht miteinander koppeln. Bei H_e handelt es sich um das Proton einer sekundären Alkoholgruppierung (bei Acetylierung Verschiebung um 1 ppm nach tieferem Feld), H_d muß somit an das C, das das Ätherende des Lactons trägt, gebunden sein.

H_c ist nach seiner Verschiebung vinylischer Natur und steht, da es nur eine Aufspaltung von <1 Hz zeigt, an einer dreifach substituierten Doppelbindung. Damit läßt sich die Partialstruktur zu **B** erweitern.

Von den acht in dem Terpen enthaltenen C-Atomen können die sieben mit einem o markierten kein weiters H tragen und erscheinen in der Partialstruktur **B** auch nur einmal. Die verbleibenden H_f und H_g müssen somit einer CH_2-Gruppe angehören. Durch Doppelresonanz-

*6. Mitt. der Reihe "Inhaltsstoffe der Ordnung Celastrales". 5. Mitt. s. Ref. [1].