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TWO NEW ACETYLENIC COMPOUNDS FROM *CHRYSANTHEMUM BOREALE*

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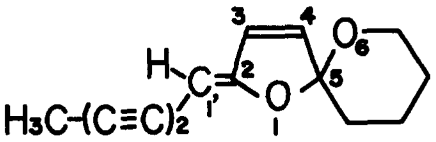
From the *Compositae* 2-(2,4-hexadiynylidene)-1,6-dioxaspiro[4.5]decene-3(I) and its derivatives have been isolated by Bohlmann et al.[1)] We have now isolated, in a course of our chemosystematic investigation on the *Chrysanthemum* native in Japan, two new acetylenic compounds from the root of *Ch.boreale* Makino (Japanese name Aburagiku) and elucidated the structures as di-acetoxy(II) and hydroxy-isovaleryloxy(III) derivatives of the dioxaspiro[4.5]decane.
The present letter deals with evidences for the structural determination of these compounds.

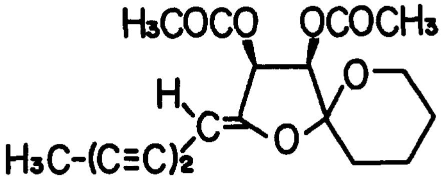
The first compound(II), $C_{18}H_{20}O_6$(M^+ 332.1312); mp 118-119°; $[\alpha]_D$ -5.6° (0.37% in $CHCl_3$), was isolated as a major component from an ether extract of the root by means of repeating column chromatography over silica gel.
The spectral evidences indicated the compound to contain two secondary acetoxy groups($\nu_{max}^{CCl_4}$ 1760, 1230, 1050 cm^{-1}; $\delta_{ppm}^{CCl_4}$ 2.08, 2.10, each 3H, s; δ 4.99, 1H, d, J=7.5; δ 6.07, 1H, d.d, J=7.5, 2.0), and the hydrolysis of the compound with methanolic KOH furnished a glycol(IV), $C_{14}H_{16}O_4$(M^+ 248.1036); mp 146-147°; $[\alpha]_D$ +112° (0.37% in $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3550, 3400, 2230, 2150, 2030, 1650, 1110, 1070, 970, 890 cm^{-1}; $\delta_{ppm}^{CDCl_3}$ 1.97, 3H, d, J=1.2; δ 3.80, 1H, d, J=6.5; δ 4.84, 1H, d.d, J=6.5, 2.0; δ 5.08, 1H, d.q, J=2.0, 1.2.

Besides, it contained such several groups as a vinylic proton(ν 1665, 885; δ 5.03, 1H, d.q, J=2.0, 1.0), an acetylenic methyl(ν 2230, 2150, 2040; δ 1.97, 3H, d, J=1.0), an oxygen-adjacent methylene(δ 3.73, 2H, t, J=5.0) and three methylenes(δ 1.50-1.90, 6H). The signal pattern of the NMR spectrum suggested a long range coupling between the vinylic proton and the acetylenic methyl, and the irradiation on the vinylic proton, in fact, reformed the doublet of the acetylenic methyl into a singlet. The UV spectrum, λ_{max}^{EtOH} 217 nm(log ε 4.53), 224(4.69), 250(4.02), 263(4.24), 278(4.39) and 293(4.31), revealed the existence of a conjugated diyne-ene system,$^{2)}$ and also the compound took up five molar equivalents of hydrogen on catalytic hydrogenation over PtO_2 in AcOH to give a saturated decahydro derivative(V), $C_{18}H_{30}O_6$(M^+ 342.2056); $\nu_{max}^{CCl_4}$ 1750, 1230, 1050 cm^{-1}; $\delta_{ppm}^{CCl_4}$ 0.91, 3H, t, J=6.0. These evidences indicate that the compound contains a partial structure of $H_3C\text{-}(C{\equiv}C)_2\text{-}CH{=}C{<}$. By comparative inspection between the molecular formula and the above mentioned evidences, the structure of the first acetylenic compound could be reasonably characterized as a 2-(2,4-hexadiynylidene)-3,4-diacetoxy-1,6-dioxaspiro[4.5]decane(II), the structure of which was confirmed by a decoupling experiment and the derivation into the compound(I): irradiation on the center of double doublet of the secondary acetoxy methine(δ 6.07) reformed the doublet of the other acetoxy methine(δ 4.99) into a singlet and the double quartet of the vinylic proton(δ 5.03) into a quartet(J=1.0) leaving the long-range coupling with the acetylenic methyl proton intact, and irradiation on δ 4.99 reformed the double doublet at δ 6.07 into a doublet(J=2.0) leaving the coupling with the vinylic proton intact. On the other hand, the glycol(IV), after being converted into a ditosylate, was heated with NaI and Zn in dimethyl formamide$^{3)}$ to give the compound(I) as a main product, the identity of which was confirmed by comparison with the authentic sample on TLC and spectrometries.$^{4)}$

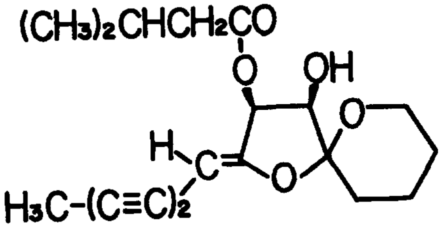
The second compound(III), $C_{19}H_{24}O_5$(M^+ 332.1524), mp 88-89°; $[\alpha]_D$ +77.4° (0.49% in $CHCl_3$), was isolated as a minor component. The UV spectrum, λ_{max}^{EtOH} 217 nm(log ε 4.49), 225(4.69), 252(4.18), 264(4.41), 278(4.53) and 293 (4.45), resembled closely to that of the first compound. Although, in this compound, the two secondary acetoxy groups present in the first compound were replaced by a secondary isovaleryloxy group($\lambda_{max}^{CCl_4}$ 1760, 1190, 1385, 1375 cm^{-1}; $\delta_{ppm}^{CCl_4}$ 5.91, 1H, d.d, J=7.4, 2.0; δ 1.01, 6H, d, J=6.7) and a secondary hydroxyl group(ν 3575, 3500; δ 2.52, 1H, exchangeable with D_2O; δ 3.68, 1H, d, J=7.4), the remaining groups of a vinylic proton(ν 1665, 885; δ 4.98, 1H, d.q, J=2.0, 1.0), an acetylenic methyl(ν 2250, 2150, 2050; δ 1.95, 3H, d, J=1.0), an oxygen-adjacent methylene(δ 3.82, 2H, t, J=5.0) and three methylenes(δ 1.50-1.90, 6H) were in common with the first compound. Besides, the hydrolysis of the compound with methanolic KOH furnished the glycol(IV) and isovaleric acid in a good yield, which were identified by spectrometries. These evidences revealed the compound to be a mono-isovaleryl ester of the glycol(IV).



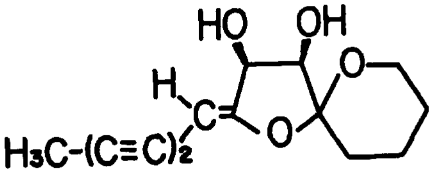
(I)



(II)



(III)



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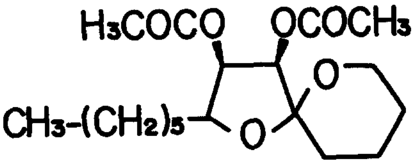
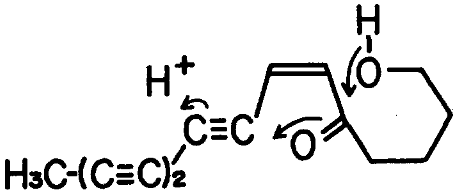


(V)



(VI)

Irradiation on the center of the double doublet of the secondary isovaleryloxy methine(δ 5.91) reformed the doublet at δ 3.68($H-\overset{|}{\underset{|}{C}}-OH$) into a singlet and the double quartet of the vinylic proton(δ 4.98) into a quartet (J=1.0) leaving the coupling with the acetylenic methyl intact. Thus, the second compound should be characterized as 3-isovaleryl ester(III) of the glycol(IV). Furthermore, the coupling constants of vicinal protons between C_3-H and C_4-H were respectively 7.5, 7.4 and 6.5 Hz in the first compound, second compound and glycol. The values indicate these compounds to take the cis-configuration at the positions of C_3 and C_4. The coupling constant between the vinylic proton($C_{1'}$-H) and its allylic proton(C_3-H), which was 2.0 Hz in the above three compounds, also reveals that the double bond hold the *seqcis* or *Z* configuration on these compounds.[1,5] Accordingly, the stereochemistry of these compounds except the spiro center should be represented by II, III and IV, respectively.

These acetylenic compounds(II and III) may be biosynthesized by oxidation and esterification of the compound(I) derived from a long chain-precursor(VI) by oxidative cyclization.

References

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