Structure of Fibleucin, a New Furanoid Diterpene

By Kazuo Ito and Hiroshi Furukawa*

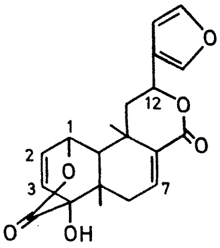
(*Faculty of Pharmacy, Meijo University, Yagoto, Showa-ku, Nagoya, Japan*)

Summary The structure of fibleucin, a new furanoid diterpene, is shown to be (I).

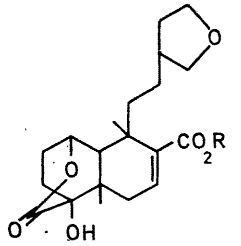
From the extract of *Fibraurea chloroleuca* Miers (Menispermaceae), we isolated a new furanoid diterpene, fibleucin, in addition to a known diterpenoid, fibraurin.[1] The structure (I) is assigned to fibleucin on the basis of chemical and spectral studies.†

Fibleucin‡: $C_{20}H_{20}O_6$ (M^+ m/e 356), m.p. 169—172°, $[\alpha]_D$ $-$ 28° (pyridine), λ_{max} 208 (ϵ 11,200) and 230 nm. (ϵ 7900); ν_{max} (Nujol) 3440 (OH), 3100, 1500, 915, 875 (furan), 1760, 1705 (two δ-lactones), and 1630 cm.$^{-1}$ (double bond). The n.m.r. spectrum [in $(CD_3)_2SO$] shows two tertiary methyls (0·95, 1·20, two singlets), a β-monosubstituted furan (6·63, 1H, β-proton, and 7·72, 2H, α-protons), a tertiary hydroxy-group (6·20, 1H, singlet, disappeared on D_2O exchange), a trisubstituted double bond (7·28, 1H, quartet, J 3·5, 8·0 c./sec.) adjacent to a methylene group, and a proton at C-12 as the X part of an ABX system (5·67, 1H, quartet, J 3·5, 11·5 c./sec.).

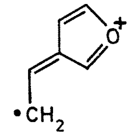
Hydrogenation of (I) with Pd–C in methanol gave a carboxylic acid (II), ν_{max} 3500, (OH), 1750 (δ-lactone),



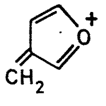
(I)



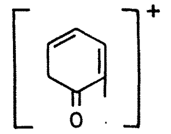
(II) R=H
(III) R=Me



a



b



c

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† Unless otherwise specified, all i.r. spectra were obtained in chloroform solution. N.m.r. spectra were measured in deuteriochloroform and the chemical shifts are expressed in p.p.m. from Me_4Si.

‡ The homogeneity of all compounds was evaluated by t.l.c. and by n.m.r. spectroscopy.

1690 ($\alpha\beta$-unsaturated CO_2H), and 1630 cm.$^{-1}$ (·C:C·), which had n.m.r. ($CDCl_3$) bands at 1·27 (6H, singlet, two tertiary methyls), 6·00 (1H diffuse singlet, CO_2H), and 7·00 (1H, triplet, J 5·0 c./sec.). Catalytic hydrogenolysis of a lactone allylically situated to a furan ring is well documented.[2] The position of the trisubstituted double bond was defined by the i.r. and n.m.r. spectra of the acid (II) and its methyl ester (III): ν_{max} 3500 (OH), 1750 (δ-lactone), 1712 ($\alpha\beta$-unsaturated ester), and 1630 cm.$^{-1}$ (·C:C·); n.m.r. spectrum (in $CDCl_3$) τ 1·27 (6H, singlet, two tertiary methyls), 3·73 (3H, singlet, OCH_3), and 6·80 (1H, triplet, J 5·0 c./sec.).

In the n.m.r. spectrum [in $(CD_3)_2SO$] of fibleucin, another ABX type pattern (6·56, 1H, quartet, J 5·0, 8·0 c./sec., 2-H; 6·22, 1H quartet, J 2·0, 8·0 c./sec., 1-H; 5·38, 1H, quartet, J 2·0, 5·0 c./sec., 3-H) is observed, similar to the one in the n.m.r. spectrum of columbin in the same solvent, showing the presence of the ring-A lactone moiety. The existence of this system in fibleucin is supported by its ready decarboxylation.

The structure assigned to fibleucin (I) is also supported by the mass spectrum. The predominant fragmentation of the molecular ion (m/e 356) gives the ion at m/e 312 ($M^+ - CO_2$) as the base peak. Other intense peaks at m/e 94 and 81 are assigned to the ions *a* and *b*, respectively, in accord with similar furan lactones.[1,3] A characteristic peak at m/e 108 is assigned to the ion *c* which arises from the ion at m/e 312 ($M^+ - CO_2$) by the *retro*-Diels–Alder-type fragmentation of ring B.

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[1] *cf.* T. Hori, A. K. Nakanishi, S. Sasaki, and M. C. Wood, *Tetrahedron*, 1967, **23**, 2649.

[2] W. R. Taylor and C. R. Willis, *J. Chem. Soc.* (*C*), 1968, 2781.

[3] R. I. Reed and W. K. Reid, *J. Chem. Soc.*, 1963, 5933; G. A. Santos, *Chem. and Ind.*, 1965, 1074; W. R. Chan, D. R. Taylor, and C. R. Willis, *J. Chem. Soc.* (*C*), 1968, 2781.