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CRYSTAL AND MOLECULAR STRUCTURE OF JOLKINOLIDE B, A NOVEL OXIDOLACTONE DITERPENE

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A crystalline oxidolactone, $C_{20}H_{26}O_4$, was isolated from Euphorbia Jolkini Boiss, and called jolkinolide B. The structure of jolkinolide B was reported[1] on the basis of chemical reactions and spectroscopic evidence. The structural elucidation by X-ray crystallography of jolkinolide B was undertaken to determine the detailed configuration and to observe the bonding system of oxidolactone group[2]. Now, we wish to report the results of X-ray analysis and the growth inhibition of jolkinolide B to cultured Hela cell.

The recrystallization of jolkinolide B from acetone gave well formed, colourless, and monoclinic crystals. The space group is $P2_1$ and the lattice constants are a= 12.09 Å, b= 10.75 Å, c= 6.91 Å, and β= 103.2°. The final R index for 1756 reflections is 0.08. A view of the molecule and the stereochemistry of jolkinolide B (1) is shown in the Figure,

The absolute configuration at C-5 and C-10 agrees with the result which was determined by chemical transformation of jolkinolide B to (-)-ferruginol[3]. A planar zig-zag conformation of $H\text{-}C_9\text{-}C_8\text{-}C_{14}\text{-}H$ accounts for the long-range coupling between H-9 and H-14 ($J < 1.0$ Hz), which has been confirmed by the decoupling procedure in the NMR spectrum of jolkinolide B. The β-configuration of two epoxides in ring C conformationally fixed to the boat-form is consistent with the result from epoxidation of jolkinolide A (2) with m-chloroperbenzoic acid. The presence of 1,4-dioxaspiro[2,4]hept-6-en-5-one system makes the epoxide ring in oxidolactone very distorted. Bond angles and bond lengths of two epoxides in jolkinolide B are summarized in the Table. The growth inhibition of jolkinolide B to cultured Hela cell was examined and ID_{50} of jolkinolide B was 2.3 μg/ml. Further investigation about physiological activities of jolkinolide B are in progress.

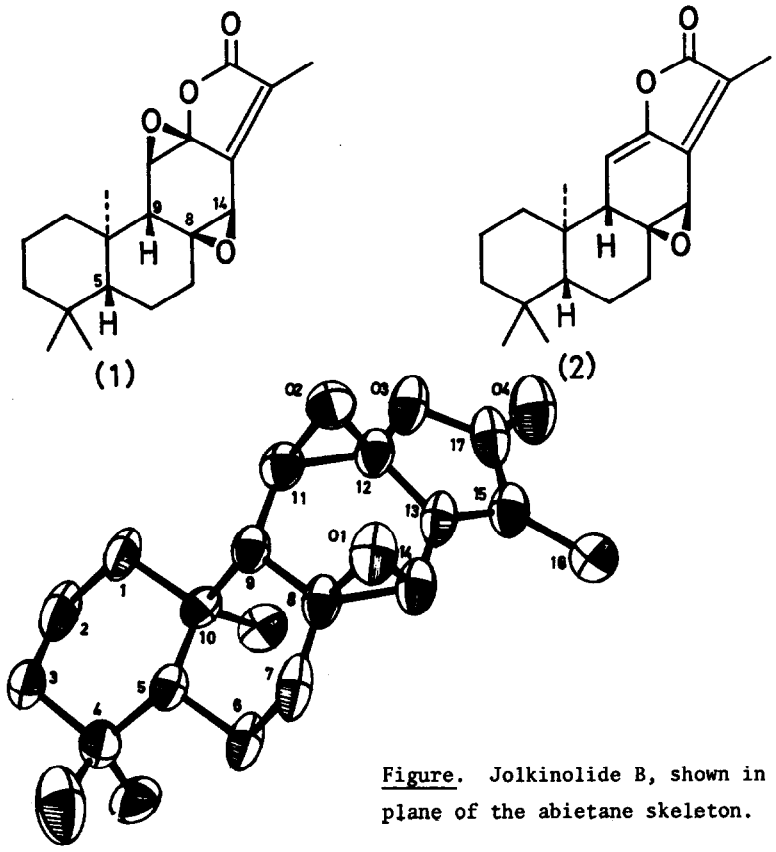

Figure. Jolkinolide B, shown in the best plane of the abietane skeleton.

Table. Bond angles and bond lengths of two epoxides in jolkinolide B.

Bond Angles		Bond Lengths	
C8-C14-O1	58.7°	C8-C14	1.51 Å
C14-C8-O1	58.2	C8-O1	1.44
C8-O1-C14	63.1	C14-O1	1.44
C11-C12-O2	61.3	C11-C12	1.46
C12-C11-O2	57.4	C11-O2	1.46
C11-O2-C12	61.3	C12-O2	1.40

REFERENCES

1) D. Uemura and Y. Hirata, Tetrahedron Letters, 1387 (1972); D. Uemura and Y. Hirata, Chemistry Letters, 819 (1974).

2) R.D. Hoffsommer, H.L. Slates, D. Taub, and N.L. Wendler, J. Org. Chem., 27, 353 (1962).

3) C.W. Brandt and L.G. Neubauer, J. Chem. Soc., 1939, 1031; C.H. Brieskorn, A. Fucks, J.B. Brendenberg, J.D. MaChesney, and Wenkert, J. Org. Chem., 29, 2293 (1964).