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STRUCTURE OF INUMAKILACTONE D

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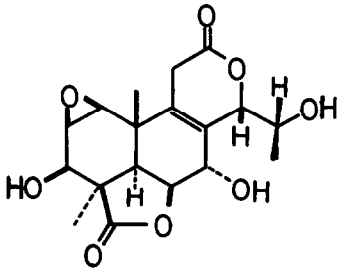
Previously we have reported the isolation of inumakilactones A, B and C, nagilactone C, and ponasterone A from the seeds of Podocarpus macrophyllus D. Don (1). Continuous investigation of the constituent of the seed of the same plant led to the isolation of a new norditerpene lactone, named inumakilactone D, as a minor constituent.

Inumakilactone D, $C_{18}H_{22}O_8$, m.p. 263-5° (decomp.) showed the following spectra (2): ν^{KBr} 3300, 1760 and 1700 cm^{-1}, δ^{DMSO-d_6} 0.86 (3H, s), 1.00 (3H, d, J=6.5), 1.32 (3H, s), 2.06 (1H, d, J=6.5), 3.06 (1H, br.d, J=22), 3.2-3.4 (2H), 3.65 (1H, br.d, J=22), 4.00 (1H, m), 4.25 (1H, d, J=5.5), 4.5-4.7 (2H), 5.00 (1H, d, J=3). These spectral data are characteristic of the norditerpene lactones (3) having hydroxyl, γ-lactone, and δ-lactone groupings. Since the amount of material available was limited, compound was subjected to X-ray analysis, which eventually established the structure shown.



A single crystal, recrystallized from methanol, belongs to space group $P2_1$ with cell dimensions of $a=10.025_2$, $b=11.145_2$, $c=7.403_1$ Å, $\beta=97.63_3°$, and Z=2. A total of 1561 reflections within $2\theta=140°$ was collected on an automated four-circle diffractometer using Cu-Kα radiation. The structure was solved by direct method on the basis of multisolution tangent formula refinements coupled with the aid of techniques involving negative quarted interactions (4). Refinement was carried out for C and O atoms using

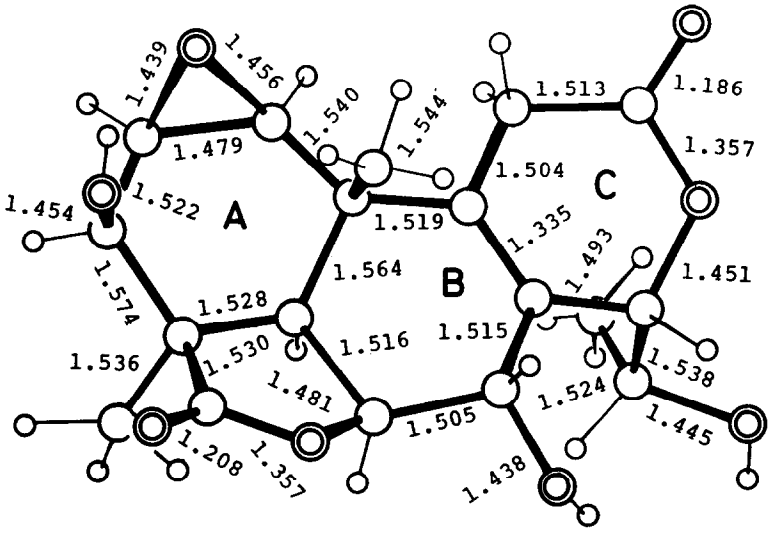


Fig. I

the block-diagonal least-squares methods with anisotropic temperature factors. All hydrogen atoms were located by the difference Fourier synthesis and included isotropically in the refinement. Final R value was 0.059 for the observed reflections. A perspective drawing of the molecule together with all interatomic distances is shown in Fig. I. All the distances as well as the bond angles are normal. Rings A, B, and C assume boat, twisted boat, and twisted boat conformations, respectively. In any event, the structure of inumakilactone D was established beyond any doubt.

References and Footnote

1) S. Itô, M. Sunagawa, M. Kodama, H. Honma and T. Takahashi, Chem. Commun., 91 (1971).

2) M.p., IR absorptions and NMR spectra previously reported for inumakilactone C were found to be those of inumakilactone D. Correct data of the former compound will appear in our future publication.

3) S. Itô and M. Kodama, Heterocycles, 4, 595 (1976).

4) G.T. de Titta, J.E. Edmonds, D.A. Langs and H. Hauptman, Acta Cryst., A31, 472 (1975).