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STRUCTURE OF A NEW DAPHNIPHYLLUM ALKALOID, DAPHNILACTONE A

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Daphnilactone A[1] was a minor component of the alkaloids, isolated from Daphniphyllum macropodum Miquel (yield: ca. 0.00001%). The spectral data[2] of daphnilactone A revealed the presence of an isopropyl group (δ 0.91, 0.93ppm, each 3H, d, J=6Hz), a tertiary methyl group (δ 1.05, 3H, s), and a δ-lactone ring (ν_{max} 1737cm^{-1}). The difficulty in clarifying this structural feature with chemical methods and the complexion of the structure stimulated us to the present X-ray crystallographical study. We have determined the crystal structure of this compound by the direct phase determination method, because of its small quantity.

Daphnilactone A, $C_{23}H_{35}O_2N$ (MW. 357.5), m.p. 194.5-195.5°, was crystallized from a mixture of benzene and n-hexane as colorless needles elongated along the c-axis, which were shown to be orthorhombic with unit cell dimensions of a=14.258, b=13.481, c=10.090Å and belong to space group $P2_12_12_1$. The density measured by the flotation method using a mixture of n-hexane and carbon tetrachloride is 1.14g.cm^{-3}, which agreed with the calculated value of 1.13g.cm^{-3} based on the presence of four molecules in a unit cell.

Lattice constants and intensities were measured at 5°C, on a Hilger and Watts four-circle automatic diffractometer Y-290 with Cu-Kα radiation. A total of 2014 independent non-zero intensities were collected in the range, $\theta \leq 70°$. The structure was solved by usual symbolic addition procedure.[3,4] Refinement of the structural parameters was carried out by the block-diagonal least-squares calculations with anisotropic thermal parameters except the hydrogen atoms, and with isotropic thermal parameters for hydrogen atoms, and the R factor was 0.058.

The molecular shape of daphnilactone A is shown in Fig. 1.

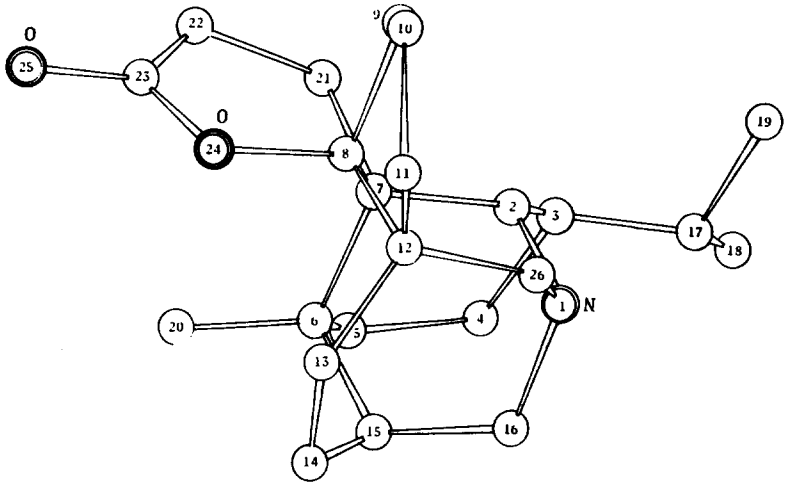
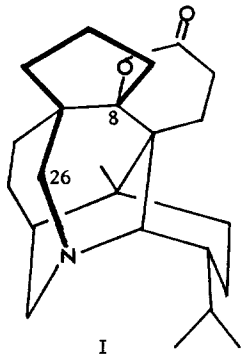


Fig. 1



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The ring system of daphnilactone A is a nolel one, but it has also a 2-azabicyclo[3,3,1] nonane ring, which is a common moiety in daphniphyllum alkaloids.

Generally from a structural point of view, daphniphyllum alkaloids can be classified into three groups (the daphniphylline[5], and yuzurimine[6], and secodaphnipylline[7] groups), this alkaloid belongs to a new group. The structure is heptacyclic and four rings (δ-lactone, cyclopentane, piperidine, and cycloheptane) have the C(8)-atom in a common giving a complex spiro-system.

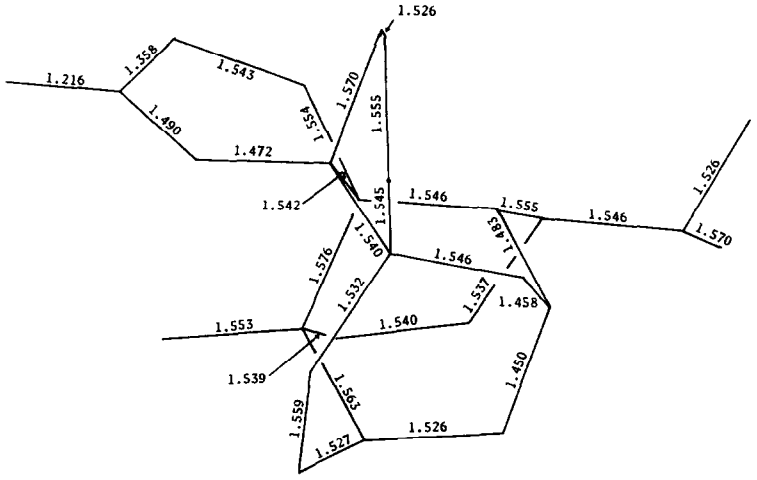


Fig. 2 Bond lengths (Å) of daphnilactone A. The range of their e.s.d.'s is 0.005 - 0.007Å.

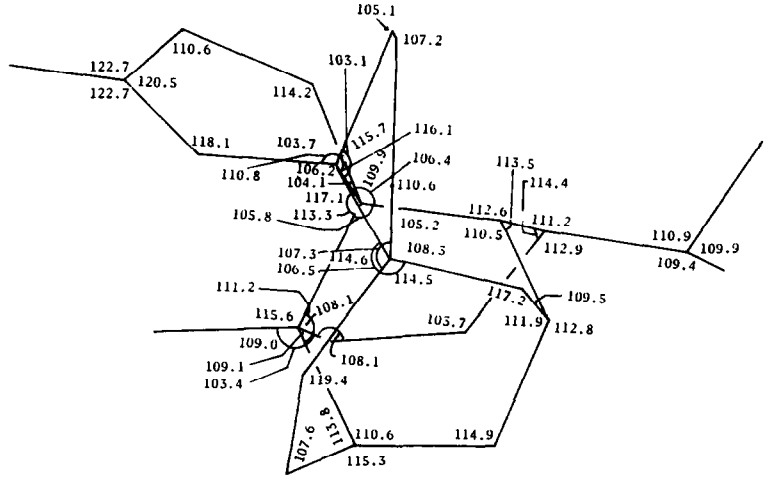
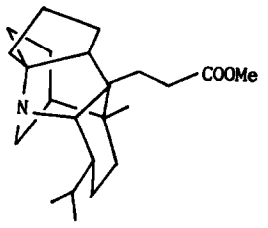


Fig. 3 Bond angles (°) of daphnilactone A. Their e.s.d.'s vary between 0.5 - 0.7°.

The skeleton of daphnilactone A are considered to be constructed by the insertion of C_1-unit [C(26)] into a nitrogen-carbon bond in the daphniphylline group [ex. methyl homodaphniphyllate(II)[8]] and by its lactonization, by comparison with the structures of daphniphyllum alkaloids.



II

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1) This alkaloid corresponds to alkaloid C in the preliminary communication [M. Toda, H. Irikawa, S. Yamamura, and Y. Hirata, Nippon Kagaku Zasshi, 91, 103 (1970)].

2) NMR spectrum was measured at 60MHz in $CDCl_3$ with TMS as the internal standard, and IR spectrum in KBr disk.

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