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STRUCTURE OF A NEW DAPHNIPHYLLUM ALKALOID, DAPHNILACTONE B

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Daphnilactone B[1] was a major component of the alkaloids, isolated from the fruits of Daphniphyllum macropodum Miquel. This alkaloid has never been isolated from other parts of this plant. The spectral data[2] of daphnilactone B showed the presence of a secondary methyl group (δ 1.00ppm, 3H, d, J=6Hz), a vinyl proton (δ 5.67, 1H), and a lactone ring (ν_{max} 1726cm^{-1}). The difficulty in clarifying this structure with chemical methods and the interest in the biogenesis of the daphniphyllum alkaloids stimulated us to the present X-ray crystallographical study. We have established the crystal structure of this compound by the direct phase determination method, because of its small quantity.

Daphnilactone B, $C_{22}H_{31}O_2N.1/2C_6H_6$ (MW. 380.5), m.p. 92-94°, was crystallized from a mixture of benzene and n-hexane as colorless plates, which were shown to be tetragonal with unit cell dimensions of a,b=8.580, c=55.529Å and belong to space group $P4_12_12$ (or $P4_32_12$). The density measured by the flotation method using a mixture of n-hexane and carbon tetrachloride is 1.24g.cm^{-3}, which agreed with the calculated value of 1.24g.cm^{-3} based on the presence of eight molecules and four solvating benzene molecules in a unit cell.

Lattice constants and intensities were measured at 5°, on a Hilger and Watts four-circle automatic diffractometer Y-290 with Ni filtered Cu-Kα radiation. A total of 1903 independent non-zero intensities were collected in the range $\theta \leq 70°$. The structure was solved by the symbolic addition procedure.[3] The solvating benzene molecule was found on a twofold axis. Refinement of the structural parameters was carried out by the block-diagonal least-squares calculations with anisotropic thermal parameters and the hydrogen atom contributions were included in the structure factor calculations. The final R value was

0.095. The molecular shape of daphnilactone B is shown in Fig. 1.

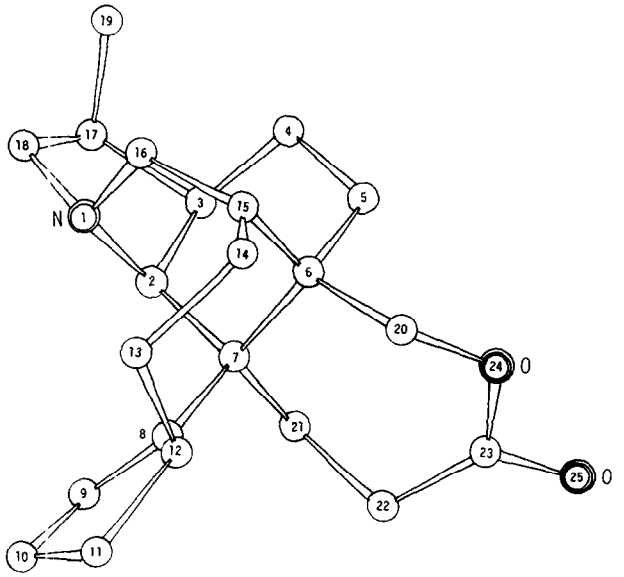
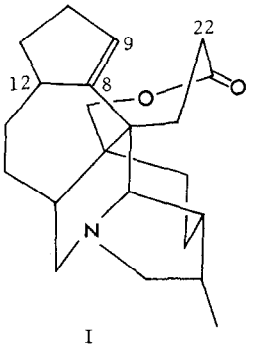


Fig 1



I

The ring system of daphnilactone B is a novel one, but it has also a 2-azabicyclo[3, 3,1]nonane ring, which is a common moiety in the daphniphyllum alkaloids. Further this structure has a seven-membered lactone ring and a cyclopentene ring with C(8)-C(9) double bond.

From the structural point of view, daphniphyllum alkaloids can be classified into four groups (the daphniphylline,[4] yuzurimine,[5] secodaphniphylline,[6] and daphnilactone A[7]

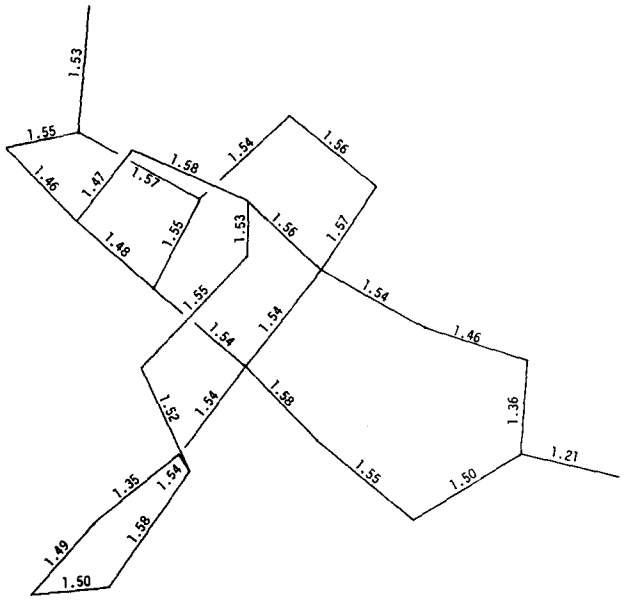


Fig. 2 Bond lengths (Å) of daphnilactone B. The range of their e.s.d.'s is 0.009 - 0.013Å.

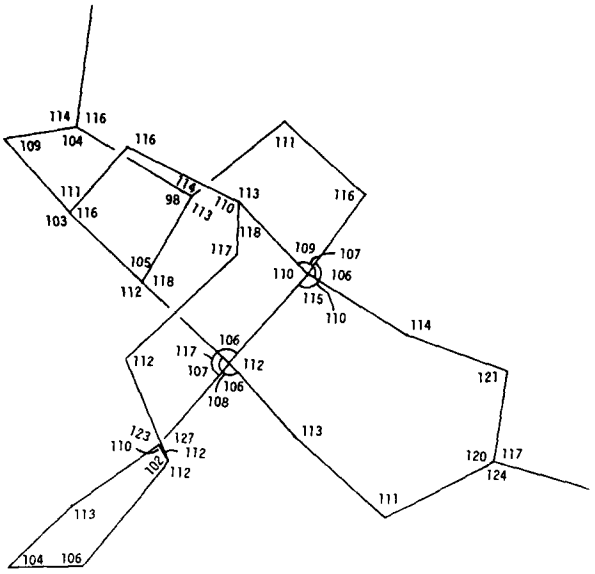
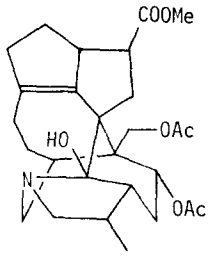


Fig. 3 Bond angles (°) of daphnilactone B. Their e.s.d.'s vary between 0.5 - 0.7°.

groups), this alkaloid belongs to a fifth group.

From a biogenetic point of view, we consider that daphnilactone B has a close relationship to yuzurimine(II). The carbon skeleton of the alkaloid is correlated to one of the yuzurimine group as a result of the C(8)-C(22) bond formation and the double bond migration from C(8)-C(9) to C(8)-C(12).



II

All computations were performed on a FACOM 230-60 at Nagoya University Computation Center using our programs.

REFERENCES

1 The isolation and chemical properties of daphnilactone B will be reported in detail.

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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