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ISOLATION AND THE STRUCTURE OF METHYL HOMODAPHNIPHYLLATE, A PLAUSIBLE INTERMEDIATE BETWEEN DAPHNIPHYLLINE AND YUZURIMINE

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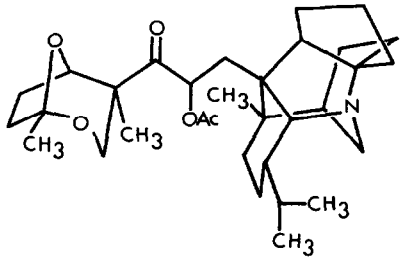
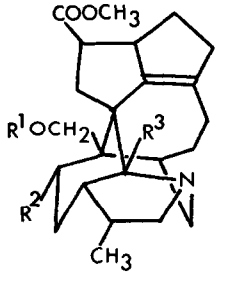
In the previous paper (1), we reported the structures of several alkaloids which were isolated from the bark and leaves of Daphniphyllum macropodum Miquel (2). These alkaloids are structurally divided into two groups, daphniphylline (I) and yuzurimine (II), the main carbon skeleton of which consists of four isoprene units and an acetate. In order to find biogenetic intermediates between daphniphylline (I) and yuzurimine (II), we further examined alkaloidal components of the fruit of the above plant and could isolate five alkaloids in a pure form, as described below.

The fruit of Daphniphyllum macropodum Miquel was extracted with methanol to give a resinous substance, from which five alkaloids were isolated by repeated column chromatography on basic alumina (Nakarai Co. Ltd., 300 Mesh) using the



(I)

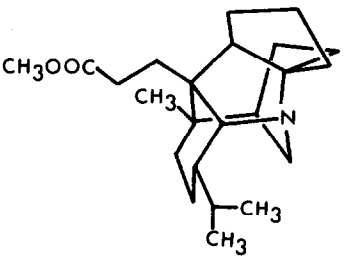


(II) R^1= Ac, R^2= OAc
R^3= OH

(III) R^1= H, R^2= H
R^3= H

mixed solvent (n-hexane : diethyl amine = 100 : 0.5). The order of elution is shown below: methyl homosecodaphniphyllate,* a new alkaloid, daphniphylline (I), yuzurimine (II) and yuzurimine B (III). The new alkaloid (as a hydrochloride) was recrystallized from MeOH - Et_2O to give colourless needles, m.p. 233 - 234° (in a sealed tube), having a molecular formula ($C_{23}H_{37}O_2N$ HCl; m/e 359 (M^+), 344, 328, 317, 286, 276 and 272; ν_{max}^{KBr} 2750 - 2400 br. and 1735 cm^{-1} This compound was identical (m.p., IR and mass spectra) with methyl homodaphniphyllate (IV), which was derived from daphniphylline (I) according to the following procedures: 1) Hydrolysis with 0.6N NaOH, 2) $NaIO_4$ oxidation, 3) $NaBH_4$ reduction, 4) Tosylation with TsCl - Py, 5) Cyanation with KCN, 6) Hydrolysis with 6N HCl and 7) Esterification with 20% HCl - MeOH (3).

From a biogenetic point of view, methyl homodaphniphyllate (IV) is regarded as one of plausible intermediates between daphniphylline (I) and yuzurimine (II).



(IV)

Melting points are uncorrected. All compounds gave satisfactory physical data.

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* Physical and chemical properties of methyl homosecodaphniphyllate has been reported (see the reference 3).

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2. Seventeen alkaloids have been isolated from the bark and leaves of the plant in our laboratory.
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