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THE NEW DAPHNIPHYLLUM ALKALOIDS, DEOXYYUZURIMINE AND ISODAPHNILACTONE-B

Shosuke YAMAMURA* and Yukimasa TERADA
Faculty of Pharmacy, Meijo University, Tenpaku-ku, Nagoya 468

Two new alkaloids, deoxyyuzurimine (2) and isodaphnilactone-B (3), have been isolated from the plant Daphniphyllaceae, and their structures also been elucidated on the basis of their spectral data. From a biogenetic point of view, particularly, the latter is interesting.

Although many alkaloids have been isolated from the plant Daphniphyllaceae,[1] such a compound as 1 has not yet been obtained. In connection with our biosynthetic and synthetic studies on these alkaloids,[2,3] we wish to describe some interesting results.

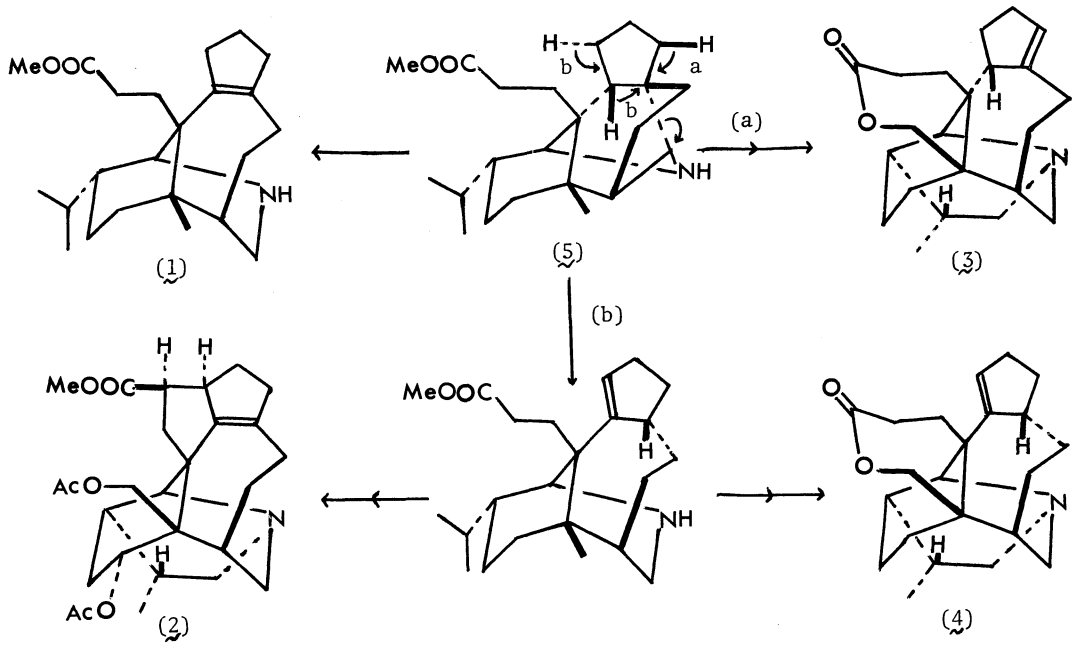
According to the same procedure as reported earlier,[4] the alkaloidal component was obtained, in ca. 0.05% yield, from the leaves of Daphniphyllum humile M. ("Ezo-yuzuriha" in Japanese) which were collected in Hokkaido (in late June). The crude mixture so far obtained was chromatographed on alumina and eluted with $CHCl_3$- benzene (2 : 1) to afford a pale brown oil, which was further separated by preparative TLC [Kieselgel PF_{254}; hexane - Et_2O - Et_2NH (10 : 10 : 1)] to give a new alkaloid, deoxyyuzurimine (2), in ca. 0.001% yield in addition to several known alkaloids[5] including secodaphniphylline and daphniteijsmine.[6] The latter has been found only in the fruits of Daphniphyllum teijsmanni Z. We further examined the alkaloidal component of this plant and could isolate another new alkaloid, isodaphnilactone-B (3), in a low yield by repeating preparative TLC [Kieselgel PF_{254}; hexane - Et_2O - Et_2NH (20 : 20 : 1)].

The new alkaloid (2) has a molecular formula [mp 132°C, $C_{27}H_{37}O_6N$ (m/e 471 (M^+))]. The IR and NMR spectra of 2 showed the presence of a sec.Me group and a carbomethoxyl group [ν_{max} 1730 cm^{-1}; δ1.06(3H, d) and 3.59(3H, s)] in addition to the following groups: AcO-CH_2-$\overset{|}{C}$- and AcO-$\overset{|}{C}$H- [ν_{max} 1750 cm^{-1}; δ4.33(2H, AB-quartet, J= 11Hz) and 5.31(1H, dd, J= 11 and 7Hz)]. These spectral data of 2 are identical with those of deoxyyuzurimine which has been already produced on zinc reduction of yuzurimine.[7]

Isodaphnilactone-B (3) is a colorless viscous liquid [$C_{22}H_{31}O_2N$ (m/e 341 (M^+)); ν_{max} 1735 cm^{-1} and no OH], which has been characterized as the corresponding methiodide [mp 196-198°C (from MeOH - Et_2O); $C_{23}H_{34}O_2NI$]. The spectral data of this new alkaloid are similar to those of daphnilactone-B (4).[8] Particularly, the NMR spectra of both compounds are quite similar to each other except for slight differences of their chemical shifts [3: δ($CDCl_3$) 1.08(3H, d, J= 7.0Hz), 2.9-3.1(2H, complex), 3.25-3.70(3H, complex), 3.75(1H, d, J= 13.0Hz), 4.50(1H, d, J= 13.0Hz) and 5.78(1H, br.s, Wh$\simeq$5Hz)].[9] From these data, clearly, this alkaloid is a double bond isomer and its structure must be depicted as 3 on the basis of the NMR signal at δ5.78, which can be assigned to the olefinic proton.[10]

Probably, daphnilactone-B and isodaphnilactone-B both are produced from such a common intermediate as methyl homosecodaphniphyllate (5), as shown in Scheme 1. Although the secondary amine (1) is considered to be present in the plant, it has not yet been found.

Scheme 1. Biogenesis of the daphniphyllum alkaloids



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References and Footnotes

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9) See the reference 8 about the NMR spectrum of daphnilactone-B.
10) The presence of a trisubstituted double bond in the seven-membered ring can be ruled out, since its NMR spectrum is expected to have a pretty broad signal assignable to the olefinic proton ($W_h \simeq 14$Hz) (see the references 3 and 8).

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