

BIOSYNTHESIS OF DAPHNILACTONE-B

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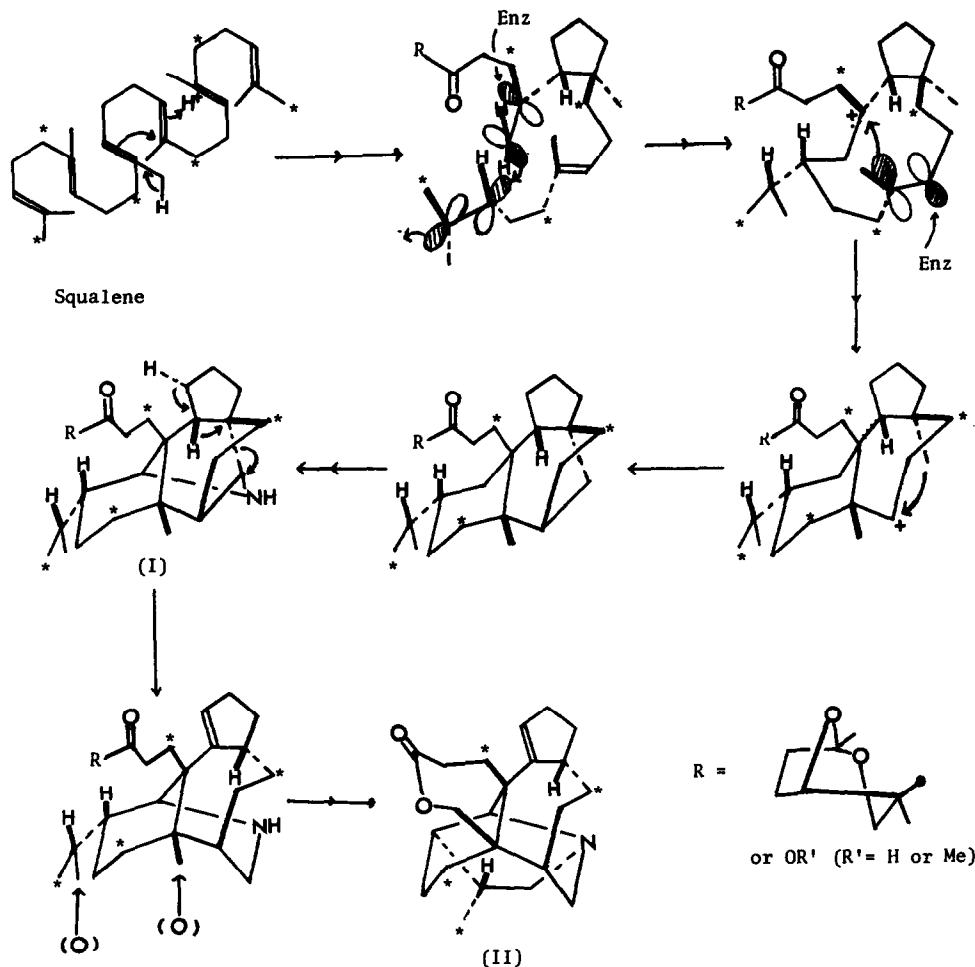
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As reported in the previous paper,¹ daphniphylline, one of the major Daphniphyllum alkaloids, has been biosynthesized from six molecules of mevalonic acid (MVA) through a squalene-like intermediate, and the highest incorporation of DL-[2-¹⁴C]MVA into daphniphylline has also been recorded in June and July (total incorporation, 0.14%). However, DL-[2-¹⁴C]MVA has not been incorporated into yuzurimine-type alkaloids, the carbon skeleton of which consists of twenty-two carbon atoms. From a biogenetic point of view, many C₂₂-alkaloids represented by yuzurimine², methyl homodaphniphyllate³, methyl homosecodaphniphyllate⁴ and daphnilactone-B⁵ could not originate from four MVA molecules and an acetate,⁶ but must be derived from such a precursor as secodaphniphylline (I) or codaphniphylline by oxidative cleavage with loss of eight carbon atoms. In the present paper, the biosynthesis of daphnilactone-B (II), a main alkaloid of the fruits of Daphniphyllum teijsmanni Zollinger,⁵ is described.

According to essentially the same procedure as reported in the previous paper,¹ the feeding experiments were carried out using a fresh spray of Daphniphyllum teijsmanni Zollinger with unripe fruits (ca. 120 grains, ca. 56g)⁷, to which DL-[2-¹⁴C]MVA (100 μCi) was fed at room temperature for 14 days. The alkaloidal components were extracted, and then carefully separated by preparative tlc [Kieselgel GF₂₅₄ nach Stahl in n-hexane-Et₂O-Et₂NH (20:20:1)] to give a radioactive fraction corresponding to daphnilactone-B (II),⁵ which was diluted with unlabelled daphnilactone-B (200mg). Recrystallization from benzene-

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7. Collected at Irako Cape (Aichi-ken, Japan) in the end of september
8. A colourless liquid (IV) $C_{23}H_{32}O_4N_2$ (m/e 400 2340), ν_{max} (film) 3360, 2190 and $1725cm^{-1}$; δ ($CDCl_3$) 1.28(3H, s), 3.03(1H, d, J= 14.0Hz), 3.50(2H, br s), 3.65(1H, d, J= 13.0Hz), 3.70(1H, brs), 4.14(1H, q, J= 14.0, 7.5Hz), 4.83(1H, d, J= 13.0Hz) and 5.83ppm (1H, br.s)
9. The ketocyanamide (V) m.p. 245-246°, $C_{22}H_{28}O_3N_2$, m/e 368(M^+) and 325, ν_{max} (KBr) 2190, 1730 and $1720cm^{-1}$; δ ($CDCl_3$) 2.32(3H, s), 3.01(1H, d, J= 14.0Hz), 3.69(1H, d, J= 13.0Hz), 3.75(1H, d, J= 3.0Hz), 4.08(1H, q, J= 14.0, 7.5Hz), 4.80(1H, d, J= 13.0Hz) and 5.90ppm (1H, br s)
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