

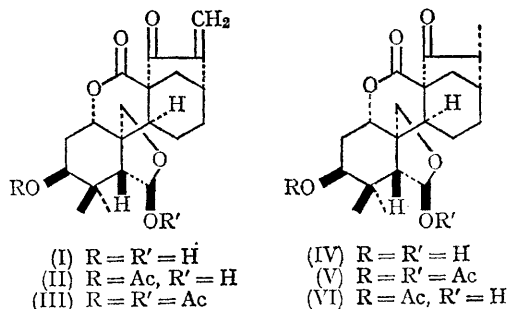
Isolation of Enmein and its 3-Acetate from *Isodon japonicus*

By EIICHI FUJITA, TETSURO FUJITA, and MASAYUKI SHIBUYA

(Institute for Chemical Research, Kyoto University, Takatsuki, Osaka-fu, Japan)

THE chemical structure and absolute configuration of enmein, a diterpenoid bitter principle of *Isodon trichocarpus* Kudo (Japanese name: "Kurobanahikiokoshi") (Labiatae), have been shown to be as in formula (I).^{1,2}

We have investigated the components of *Isodon japonicus* Hara (Japanese name: "Hikiokoshi") (dried leaves: 5 kg.) collected in Kochi prefecture, and have isolated enmein (I) (ca. 5 g.) as a major



constituent. Enmein isolated from *I. trichocarpus* is usually contaminated with dihydroenmein (IV). The n.m.r. spectrum of the enmein which was isolated from *I. japonicus*, however, showed it to be pure.

We isolated also a minor component, C₂₂H₂₈O₇, m.p. 267—271° (decomp.), [α]_D¹⁷ -112° (yield: 130 mg.). The substance contains a five-membered ring ketone conjugated with an exocyclic methylene group [λ_{max} 233 mμ (ε, 9100), ν_{max} (KBr) 1750 and 1635 cm.⁻¹, δ 5.33 and 5.99 p.p.m. (pyridine)], δ-lactone [ν_{max} (KBr) 1710 cm.⁻¹], and with a five-membered-ring hemiacetal [ν_{max} (KBr) 3400 cm.⁻¹, δ 5.82 (singlet) and 4.42 p.p.m. (pyridine) (AB type, J = 9 c./sec.)] in the molecule like enmein. Moreover, the presence of an acetyl group (which was absent in enmein) was recognized [ν_{max} (KBr) 1710 and 1265 cm.⁻¹, δ 2.19 p.p.m. (pyridine) (singlet)]. The proton signal of C-3 appeared at δ 5.07 p.p.m. overlapping with the proton signal of C-1, while that in enmein appeared at δ 3.84 p.p.m. (broad).

The foregoing data led to a presumption that the minor constituent may be enmein 3-acetate. A partial hydrolysis of enmein diacetate (III) with oxalic acid gave the 3-acetate (II),³ which was shown to be identical with the substance in question. Similarly, the dihydro-derivative of the substance proved to be identical with the known dihydroenmein 3-acetate (VI)^{1,2a,b} which was derived from dihydroenmein diacetate (V) by partial hydrolysis.

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