

While atractylodin (III), a furanoid acetylenic compound initially isolated from a Manchurian *Atractylodes* species,¹⁰ has been found in several crude drugs belonging to "Chang-zhu",¹¹ diacetyl-atractylodiol (Ia) is an only acetylenic compound elucidated in one of the crude drugs grouped in "Bai-zhu". It is worth to mention here that the elucidation of the occurrence of these two distinct acetylenic compounds in two different groups of crude drugs "Bai-zhu" and "Chang-zhu" is in good accord with a botanical diagnosis for the original plants of two groups.

Faculty of Pharmaceutical Sciences,
Osaka University,
Toneyama, Toyonaka, Osaka

ITIRO YOSIOKA
TADATO TANI
MIHOKO HIROSE
ISAO KITAGAWA

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Synthesis of (\pm)-Desmethyldecaline

Desmethyldecaline,¹⁾ an alkaloid from *Decodon verticillatus* (L.) ELL. (Lythraceae), was assigned the structure (I) based on the evidence that it was converted to decaline (II)¹⁻³ by methylation of the hydroxyl group and on the biogenetic consideration, however, the position of hydroxyl group at C-4" or C-5" has not yet been determined chemically. We tried to synthesize I in order to establish the structure of desmethyldecaline.

Benylation of the *trans*-quinolizidin-2-one (III)²⁾ with benzyl chloride gave in 83% yield the benzyl ether (IV) [m/e : 445, 443 (M^+ , 1:1), $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1} : 2790, 2760 (Bohlmann bands), 1718 (C=O)], which was reduced with the Henbest catalyst [$\text{IrCl}_4\text{-HCl-(CH}_3\text{O)}_3\text{P-iso-PrOH}$]⁴⁾ to afford the axial alcohol (V) and the equatorial alcohol (VI) in the ratio of 11:1 in 84% yield. The both alcohols (V and VI) were acetylated with acetic anhydride in pyridine to give the acetyl derivative (VII) [m/e : 447, 445 (M^+ , 1:1), δ : 5.00 (1H, m, $W_{\text{H}}=7$ Hz, CHOAc)] and the epimeric acetyl derivative (VIII) [m/e : 447, 445 (M^+ , 1:1), δ : 4.76 (1H, t-t, $J=11$; 4.5 Hz, CHOAc)], respectively.

The Ullmann condensation of VII with methyl 4-hydroxyhydrocinnamate⁵⁾ afforded the biphenyl ether (IX) [m/e : 587 (M^+), $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1} : 2800, 2770, 2740 (Bohlmann bands), 1728 (C=O)], which was hydrolyzed to furnish the hydroxy acid (X) [m/e : 531 (M^+)]. Heating of X with *p*-toluenesulfonic acid in benzene effected lactonization and debenylation, providing the lactone (I) [mp 259-261°, m/e : 423 (M^+), $\nu_{\max}^{\text{CHCl}_3}$ cm^{-1} : 3550 (OH), 2800, 2730 (Bohlmann bands), 1720 (C=O), δ : 5.20 (1H, br-s, OH), 4.86 (1H, m, $W_{\text{H}}=7$ Hz, CHOCO), 3.91 (3H, s, OCH_3)] in 37% yield, which was treated with diazomethane to afford (\pm)-decaline (II).²⁾

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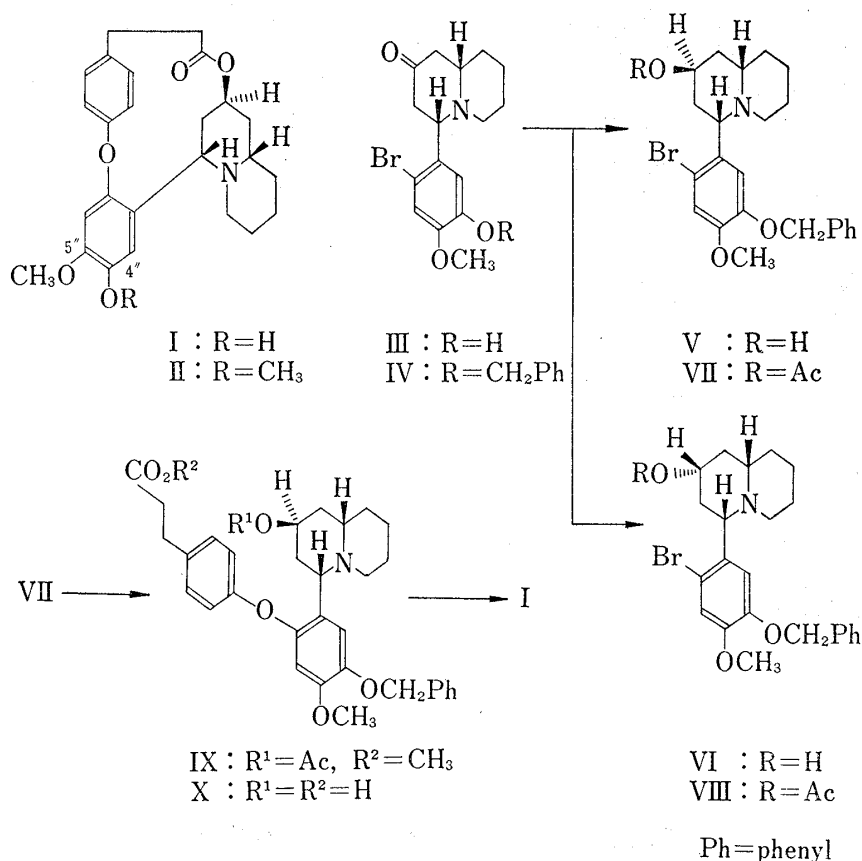


Chart 1

Though we have not yet obtained the authentic natural desmethyldecaline for the comparison with the synthetic product (I), the above-mentioned synthesis will provide a final proof for the structure of desmethyldecaline.

Faculty of Pharmaceutical Sciences
Kanazawa University
13-1, Takara-machi, Kanazawa, 920, Japan

MIYOJI HANAOKA
NOBUO OGAWA
YOSHIO ARATA

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Volatile Metabolite of Aquatic Fungi. Identification of 6-Pentyl- α -pyrone from *Trichoderma* and *Aspergillus* Species

In continuation of a study on odorous compounds which are responsible for the unpleasant taste and odor of public water supplies,¹⁾ we recently isolated two strains of fungi, a *Trichoderma* and an *Aspergillus* species, from the bottom deposits of Sengari Reservoir, Kobe City Water Supply Bureau, and their volatile metabolites were examined.

These fungi were cultured on Sabouraud agar medium (200 Petri dishes (10 cm i.d.)) at 27° for 5 days and each whole culture was submitted repeatedly to steam distillation.

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