Sodium mevalonate-2-^{14}C (50 μc., 5.85 mg.) was administered into the stem of *Dendrobium nobile* by the cotton wick method and the plant (91 g., fresh weight) was harvested after 12 days. The radioactive dendrobine obtained (12 mg.) was purified by a silica gel column chromatography using benzene-methanol (25:2) as a solvent.

The radioactivity of dendrobine was measured with a liquid scintillation counter (Tri Carb 314 EX). The specific activity was 3.68×10^5 d.p.m./m*M* and the total incorporation ratio was 0.012%. The radioactive dendrobine was then oxidized with chromium trioxide in diluted sulfuric acid to afford acetic acid. Acetic acid obtained was converted to 1-acetoamidonaphthalene and purified by sublimation and recrystallization to measure the radioactivity. The specific activity of acetic acid was 2.93×10^4 d.p.m./m*M* (95.5% of theoretical).[*1]

A sufficient incorporation of mevalonic acid-2-^{14}C into dendrobine indicates that the biosynthesis of this alkaloid proceeds through the ordinary biosynthetic pathway of sesquiterpenes.

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[*1] The theoretical specific activity of acetic acid should be 3.06×10^4 d.p.m./m*M* on the assumption that acetic acid is equally derived from the methyl and isopropyl groups of dendrobine molecule by Kuhn-Roth oxidation.

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Convenient Synthesis of 6-(1-Acetyl-2-piperidyl)-6-hydroxy-2-cyclohexene-$\Delta^{1,\alpha}$-acetic Acid γ-Lactone, the Key Intermediate in Total Synthesis of Securinine

Recently, the total synthesis[1] of securinine (I)[2] has been accomplished starting from 1,2-cyclohexanedione monoethyleneketal[3] *via* the ketol (Ⅱ)[4] and the lactone (V).[2] However, in that synthesis the yield from Ⅱ to V was only ca. 0.5%. From the preparative point of view, another better route was sought for the synthesis of V. We have now found the following new route providing V in 36.7% overall yield from Ⅱ.

The ketol (Ⅱ)[4] was brominated with bromine in glacial acetic acid at 55～65° in the presence of hydrobromic acid to give the bromo-ketone (Ⅲ), m.p. 169～170°, IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3472 (OH), 1718 (CO), 1629 (N-Ac), in 75% yield. Dehydrobromination of Ⅲ by heating with lithium bromide and lithium carbonate in dimethylformamide at 120° for

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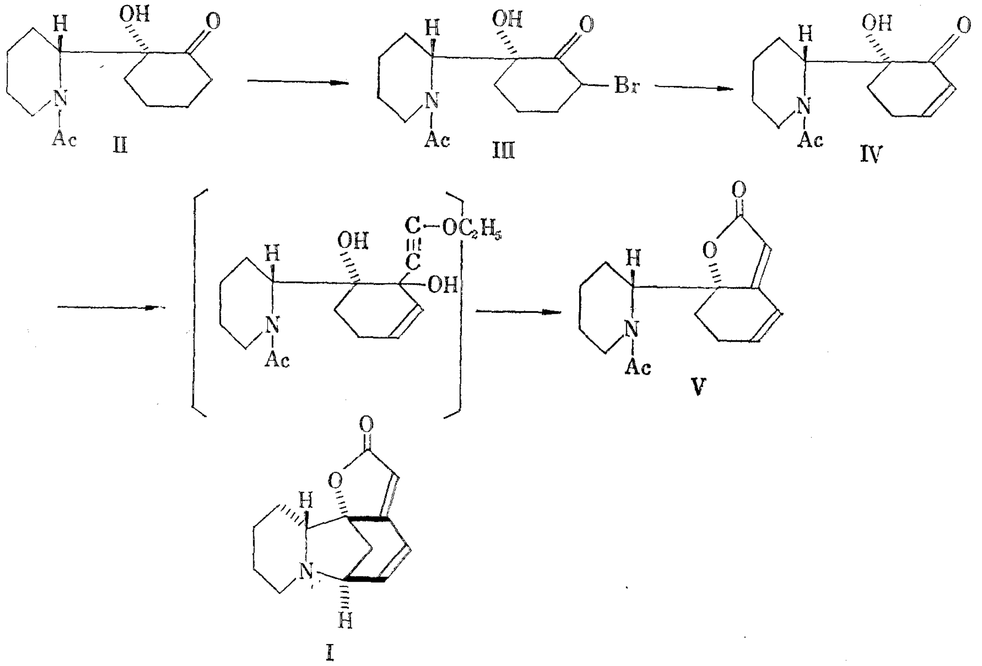

7 hours gave the unsaturated ketone (IV), m.p. 109~111°, IR ν_{max}^{KBr} cm^{-1}: 3413 (OH), 1664 (CO), 1616 (N-Ac), in 71% yield. Condensation of IV with ethoxyacetylenyl lithium in anhydrous ether at $-20\sim-30°$ gave the crude diol, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2260 ($C\equiv C$), which was refluxed with dilute sulfuric acid in tetrahydrofuran for 20 minutes to give the lactone (V), m.p. 162~164°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1739 (γ-lactone), 1634 (N-Ac), UV λ_{max}^{EtOH} mμ (log ε): 262.5 (4.17), in 69% yield. This racemic lactone (V) was identical with the degradation product (V)[2] in infrared spectrum in chloroform and in retention time on gas-liquid chromatography.

This synthesis provides the new convenient synthesis of securine.

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