Tetrahedron Letters No.6, pp. 553-555, 1967. Pergamon Press Ltd. Printed in Great Britain.

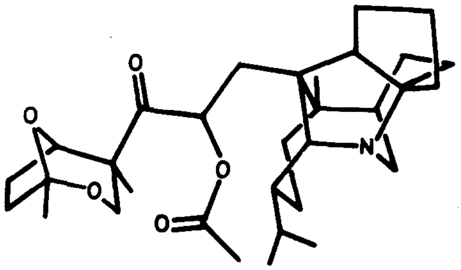
THE STRUCTURE OF CODAPHNIPHYLLINE

Hajime Irikawa, Shosuke Yamamura, Noriyoshi Sakabe, and Yoshimasa Hirata

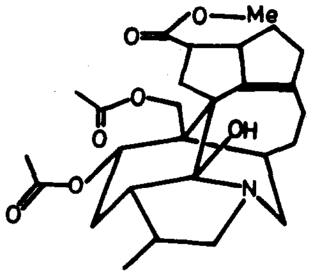
Chemical Institute, Faculty of Science, Nagoya University, Nagoya, Japan

(Received 16 November 1966)

During the course of an investigation of the alkaloids in Daphniphyllum macropodum Miquel, we reported the isolation of five new alkaloids, daphniphylline (I), yuzurimine (II), codaphniphylline (III), neodaphniphylline, and neoyuzurimine (1, 2). The structures of daphniphylline and yuzurimine were determined by the X-ray diffraction study (3, 4). On the basis of spectral data (IR, NMR, and mass spectra), the structure of third compound, codaphniphylline, has been proposed as desacetoxy-daphniphylline (2).



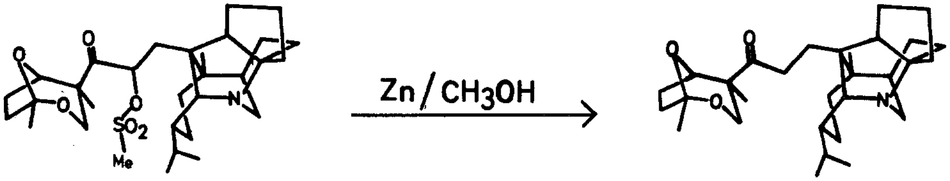
(I)



(II)

Now, we wish to report the chemical transformation from daphniphylline to codaphniphylline (5).

Hydrolysis of daphniphylline (I) with 0.6 N methanolic aqueous sodium hydroxide afforded desacetyl-daphniphylline, which was transformed by methanesulfonyl chloride in dry pyridine to the methanesulfonate (IV), m.p. 162-164 °C. The methanesulfonate was a nicely crystalline substance and had a molecular formula $C_{31}H_{49}O_6NS$ (Found: C, 66.25; H, 9.00; N, 2.30 %. Calcd.: C, 66.02; H, 8.78; N, 2.48 %), $\nu^{KBr}_{max.}$ 1720 (>C=O), 1355 and 1173 (>SO_2) cm^{-1}; $\delta^{CDCl_3}_{TMS}$ 0.86 (3H, d, J=6 c.p.s.), 0.92 (3H, s), 0.98 (3H, d, J=6), 1.12 (3H, s), 1.46 (3H, s), 2.14 (3H, s), 3.69 (1H, d, J=13), 4.30 (1H, q, J=13 and 1.6), 4.68 (1H, m), 5.81 (1H, q, J=13 and 2) p.p.m.; m/e 563 (M^+), 286, 272.



(IV) (III)

Reduction of the methanesulfonate (IV) as hydrochloride with active zinc powder in methanol gave desacetoxy-daphniphylline in 78 % yield. This compound was identified as codaphniphylline by melting point, IR and mass spectra. Therefore, the structure of codaphniphylline could unambiguously be designated as desacetoxy-daphniphylline.

These natural products are regarded as a new type of alkaloids, the main carbonskeleton of which consists of four isoprene units and one acetate.

Studies are now in progress to transform yuzurimine (II) into codaphniphylline (III).

Acknowledgements: The authors are grateful to Takeda Chemical Industries, LTD. for measurement of NMR spectra. They are also indebted to the National Institutes of Health, U.S.A., which supported this work through Grant RG-7969 and GM-7969.

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5. At first, we tried to remove the acetoxyl group of daphniphylline with active zinc powder in acetic acid under various conditions, but could not get a good result.