A Biogenetic Synthesis of (±)-Secotrinerviten-2β,3α-diol

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Based on biogenetic considerations, (±)-secotrinerviten-2β,3α-diol was synthesized from acetyl epoxy dehydromukulol (**4c**) by the action of $BF_3\cdot Et_2O$.

Termite soldiers of nastitermes genera secrete several kinds of diterpenoids as part of their defence mechanisms, of which secotrinervitanes (**1**) and (**2a**) are the typical examples.[1] These natural products are biogenetically related to cembrene A (**3a**), a trail pheromone of the termite workers:[2] bonding between C-4 and C-16‡ of the epoxy derivatives (**4a**,**b**) of (**3a**,**b**) leads to the secotrinervitane skeleton,[3] in which a macrocyclic ring is connected at the C-1 and C-4 positions of the cyclohexane ring with a *trans* diequatorial configuration.

The biological activity and particularly the unique structure

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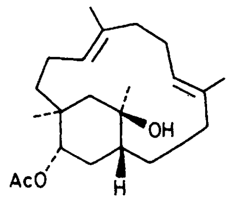
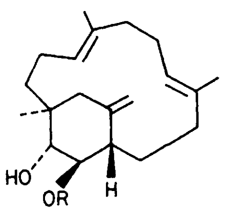
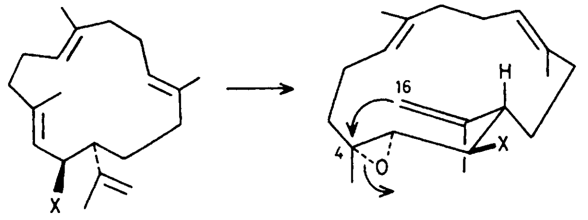
‡ Numbering is based on that of secotrinervitane skeleton.



(1)



(2) a; R = H
b; R = Ac



(3) a; X = H
b; X = OH

(4) a; X = H
b; X = OH
c; X = OAc

↓

(1) and (2a)

aroused our interest in the synthesis of these terpenoids. After completion of our synthesis of (**1**),[4] we have undertaken the biogenetic type synthesis of (±)-secotrinerviten-2β,3α-diol (**2a**)[5] starting from the epoxide (**4b**). The result is described in this communication.

In our previous paper, we reported[6] the efficient preparation of epoxy alcohol (**4b**) from *trans* dehydromukulol (**3b**). Although treatment of (**4b**) with $BF_3 \cdot Et_2O$ in diethyl ether at −40 °C resulted in the formation of a complex mixture, the corresponding acetate (**4c**), prepared from (**4b**) by the action of Ac_2O in pyridine at room temperature for 24 h, afforded the expected bicyclic hydroxy acetate (**2b**) in 82% yield when treated with $BF_3 \cdot Et_2O$ in diethyl ether at −20 °C for 17 h.§ The cyclization of (**4c**) depends largely on the solvent employed and a complex mixture was formed when CH_2Cl_2 at −78 °C was used instead of diethyl ether. Reduction of (**2b**) with $LiAlH_4$ gave free diol (**2a**). Physical data of (**2a**), thus synthesized, were identical with those of natural secotrinerviten-2β,3α-diol.

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§ (**2b**) M.p. 78—79 °C; ^1H n.m.r. ($CDCl_3$, 90 MHz) δ 5.3—5.1 (1H, m), 4.8—4.7 (1H, br.s), 4.72 (1H, d, *J* 1.5 Hz), 4.53 (1H, dd, *J* 11.3, 8.4 Hz), 3.64 (1H, d, *J* 8.4 Hz), 2.89 (1H, br.d. *J* 8.5 Hz), 2.13 (3H, s), 1.63 (3H, s), 1.57 (3H, t, *J* 1.4 Hz), and 0.87 (3H, s).