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GERMANICOL, A NEW BACKBONE REARRANGEMENT PRODUCT OF 3β,4β-EPOXYFRIEDELANE

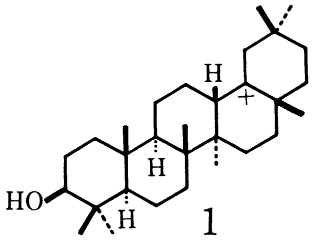
Motoo TORI, Takahiko TSUYUKI, and Takeyoshi TAKAHASHI
Department of Chemistry, Faculty of Science,
The University of Tokyo, Bunkyo-ku, Tokyo 113

Treatment of 3β,4β-epoxyfriedelane (2) with BF_3-Et_2O in benzene at room temperature gave germanicol (7; main product), besides the known rearranged products (4, 5, and 6). Germanicol is the first example of product in which a backbone rearrangement of friedelane-oleanane-type effected up to E-ring.

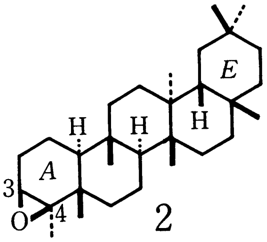
The acid-catalyzed backbone rearrangement of friedel-3-ene into olean-12-ene, olean-13(18)-ene, and into D:B-friedo-olean-5(10)-ene constitutes a model reversal of the biogenesis of friedelin from an oleanane-type intermediate (1) derived from squalene.1,2) A treatment of 3α,4α-epoxyfriedelane with stannic chloride3a) or BF_3-Et_2O3b) has been shown to yield D:B-friedo-olean-5(10)-en-3α-ol,3) olean-12-en-3α-ol,3b) 18αH-olean-12-en-3α-ol,3b) olean-13(18)-en-3α-ol,3b) and 18αH-A-neo-oleana-3(5),12-diene.3b) It has been reported that BF_3-Et_2O-catalyzed rearrangement of 3β,4β-epoxyfriedelane (2) in ether gives dendropanoxide (3), D:B-friedo-olean-5(10)-en-3β-ol (4), D:B-friedo-olean-5-en-3β-ol (5), and β-amyrin (6), besides 4α-fluorofriedelan-3β-ol.4) Thus, backbone rearrangements hitherto encountered for friedelane derivatives are limited to proceed up to A-D rings. In this communication, we wish to report the formation of germanicol (7) in the backbone rearrangement of 2.

A solution of 3β,4β-epoxyfriedelane (2; 175 mg) in benzene (150 ml) was treated with BF_3-Et_2O (1 ml) at room temperature for 10 min. After usual work-up, the reaction mixture gave a residue (ca. 170 mg), which proved by HPLC5) examination to consist of an alcohol (45 %) and of the known three rearranged products:4) D:B-friedo-olean-5(10)-en-3β-ol (4; 15 %), D:B-friedo-olean-5-en-3β-ol (5; 15 %), and β-amyrin (6; 25 %). The alcohol was separated by HPLC to afford crude crystals (ca. 30 mg), which was recrystallized from chloroform-methanol. The mp (177-178.5 °C) and spectral data6) of this alcohol were identical with those of germanicol (7).7) This received support from the following conversion: the alcohol was treated with potassium and methyl iodide under reflux to give miliacin (8),8) which was found to be identical (mp, mixed mp, IR, PMR, and mass spectrum) with an authentic specimen isolated from Panicum miliaceum L.9) When 2 was treated with BF_3-Et_2O in ether, the formation of a minute quantity of germanicol was detected.

An attack of BF_3-Et_2O to 2 would generate a cationic center at C-4 (or its equivalent species). The subsequent 1,2-shifts of methyl groups and hydrogen atoms



1



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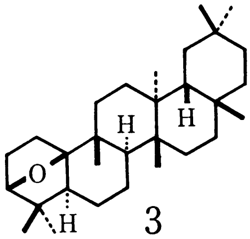

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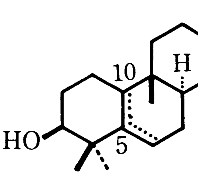
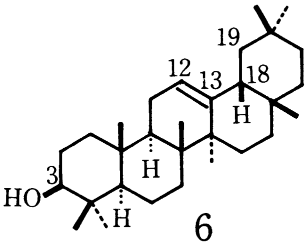


4 5(10)-ene

5 5-ene



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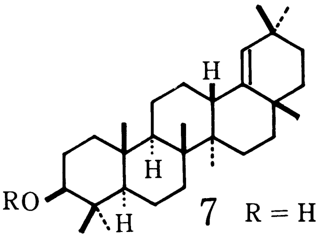

7 R = H

8 R = CH_3

would lead to the cation (1) (or its equivalent species), which on deprotonation affords germanicol (7). It is the first instance in the backbone rearrangement of friedelane-oleanane-type that the rearrangement was effected up to E-ring, and this finding is considered as a relief of the reverse direction reaction of the biogenetic process.[10)]

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5) Carried out at room temperature using a Liquid Chromatograph Model ALC/GPC 202/401 (Waters Assoc.) with an RI detector; column: μ-PORASIL 1/8 (inch) x 1 (foot); solvent system: 10 % ether-hexane; flow rate: 0.8 ml/min; pressure: ca. 450 psi.

6) IR (KBr) 3450, 1630, and 840 cm^{-1}; PMR ($CDCl_3$) δ 0.74, 0.78, 0.89, 0.98, 1.02, 1.09 (each 3H, s, t-Me), 0.94 (6H, s, 2 x t-Me), 3.20 (1H, dd, J=10 and 5 Hz), and 4.85 (1H, d, J=1.5 Hz); MS m/e (%) 426 (M^+; 50), 411 (31), 204 (100), 189 (83), and 177 (83).

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8) mp 280-281.5 °C, IR (KBr) 1635, 1180, 1110, 860, and 850 cm^{-1}; PMR ($CDCl_3$) δ 0.76 (6H, s, 2 x t-Me), 0.89, 1.02, 1.08 (each 3H, s, t-Me), 0.95 (9H, s, 3 x t-Me), 3.35 (3H, s, -OMe), and 4.85 (1H, d, J=1.5 Hz); MS m/e (%) 440 (M^+; 44), 425 (23), 393 (5), 204 (100), 189 (75), and 177 (63).

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10) Germanicol would be derived biogenetically via an oleanane-type intermediate with a cationic center at C-19.

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