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# A NOVEL FRAGMENTATION OF RING A IN 6α-HYDROXY-7-OXOABIETA-8,11,13-TRIENE AND FORMATION OF A β-NAPHTHOL DERIVATIVE

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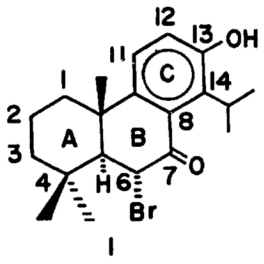
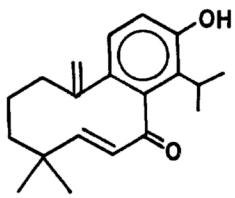
In order to examine the fragmentation reaction of tricyclic diterpenoids, 6α-hydroxy-7-oxoabieta-8,11,13-triene (V) was prepared from 7-oxoabieta-8,11,13-triene (XI) via an enol acetate (XII). After V was treated with p-toluenesulfonyl chloride, the product was heated at 200°C to afford a β-naphthol derivative (IX).

Recently, Cambie et al.[1,2] have been reported that a heterolytic fragmentation of 6α-bromo-13-hydroxy-7-oxototara-8,11,13-triene (I) with sodium hydrogen carbonate in dimethyl sulfoxide gave 7-oxo-5,10-secototara-5,8,10(20),11,13-pentaen-13-ol (II) and further treatment of the methyl ether of its mono-epoxide (III) with sulfuric acid in acetone gave an α-naphthol derivative (IV) by a cyclization-ring-opening reaction. From an examination of the above fragmentation reaction on other 6α-bromo-7-oxoditerpenoids they suggested that the structural feature of ring C necessary for secoditerpenoid (II) formation is the presence of a phenolic hydroxyl group at the C-13 position. It is of interest to study on a similar rearrangement in the case of 6α-hydroxy-7-oxoabieta-8,11,13-triene (V), which possesses no hydroxyl group at the C-13 position and, therefore, a different mode of fragmentation might be expected.

During the course of the present work, Tahara and his co-workers[3,4] reported on a direct conversion of 7-oxoabieta-5,8,11,13-tetraene (VI) to the α-acetoxynaphthalene derivative (VII) by the action of acetic anhydride and sulfuric acid, and the acetate (VII) was then converted to the methyl ether (VIII). The appearance of their work prompts us to report our own result. This communication will describe a novel fragmentation reaction of V with p-toluenesulfonyl chloride leading to a β-naphthol derivative (IX). The preparation of V was carried out as follows.




I

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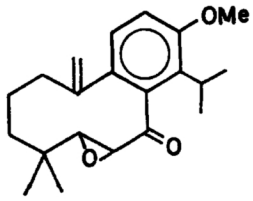


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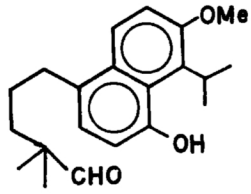


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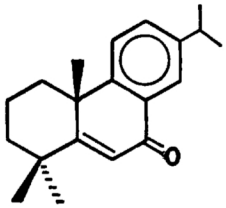
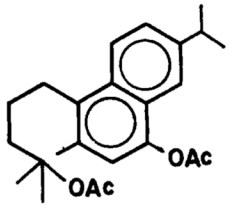
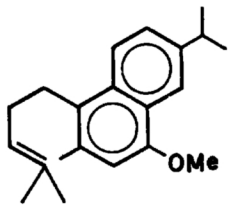



VI




VII

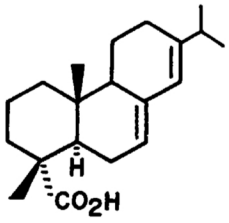



VIII

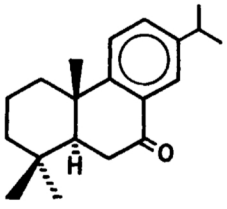
7-Oxoabieta-8,11,13-triene (XI)[5,6] derived from (-)-abietic acid (X), was treated with isopropenyl acetate in the presence of p-toluenesulfonic acid to afford the corresponding enol acetate (XII); mp 92.5-93°C; IR: 1757, 1654 $cm^{-1}$; NMR: 2.21 (d, J=2.5 Hz, $C_5$-H), 2.22 (s, -OCOC$H_3$), 5.56 (d, J=2.5 Hz, -C$H$=C-), 6.87 (bs, $C_{14}$-H). Oxidation of XII with perbenzoic acid in chloroform gave a mixture of four products which was separated by column chromatography on silica gel to give 6α-chloro-7-oxoabieta-8,11,13-triene[7] (XIII: 4% yield); IR: 1690 $cm^{-1}$; NMR: 2.10 (d, J=9 Hz, $C_5$-H), 4.40 (d, J=9 Hz, $C_6$-H), 7.53 (d, J=2 Hz, $C_{14}$-H), 6-hydroxy-7-oxoabieta-5,8,11,13-tetraene (XIV: 5% yield); IR: 3380, 1628 $cm^{-1}$; NMR: 7.08 (s, -OH, exchanged with $D_2O$), 7.91 (bs, $C_{14}$-H), V (16% yield); IR: 3475, 1667 $cm^{-1}$; NMR: 1.82 (d, J=12.5 Hz, $C_5$-H), 3.69 (bs, -OH, exchanged with $D_2O$), 4.57 (d, J=12.5 Hz, $C_6$-H), 7.83 (bs, $C_{14}$-H), and 6α-acetoxy-7-oxoabieta-8,11,13-triene (XV: 72% yield); IR: 1740, 1690 $cm^{-1}$; NMR: 2.14 (d, J=12.5 Hz, $C_5$-H), 2.17 (s, -OCOC$H_3$), 5.75 (d, J=12.5 Hz, $C_6$-H), 7.77 (bs, $C_{14}$-H). The acetate (XV) was hydrolyzed with aqueous sodium hydroxide in refluxing methanol under a stream of nitrogen to afford V (60% yield) along with XIV (12% yield) and an α-diketone derivative (XVI: 9% yield); mp 104-105°C; IR: 1715, 1673 $cm^{-1}$; NMR: 2.53 (s, $C_5$-H), 7.88 (bs, $C_{14}$-H). In the NMR spectrum of XVI, the appearance of a signal due to $C_{4\alpha}$-$CH_3$ at δ 0.40 suggests the presence of a cis A/B ring junction.[8] Treatment of XVI with boiling acetic anhydride and sodium acetate gave 6-acetoxy-7-oxoabieta-5,8,11,13-tetraene (XVII); IR: 1755, 1655 $cm^{-1}$; NMR: 2.30 (s, -OCOC$H_3$), 7.90 (bs, $C_{14}$-H), which was also obtained by a similar acetylation of XIV. Subsequently, V was treated with p-toluenesulfonyl chloride[9] in pyridine under a stream of nitrogen at 100°C for 2 hr and the mixture, after removal of the solvent (2 hr), was further heated at 200°C for 2 hr. The crude product was purified by column chromatography on silica gel to give XIV (7% yield) and a β-naphthol derivative (IX: ca. 50% yield);

IR: 3605, 3350, 1625, 1607, 1573, 1500 $cm^{-1}$; UV: $\lambda_{max}^{EtOH}$ nm (log ε) 237 (4.89), 260 (3.74), 267.5 (3.78), 286.5 (3.73), 297.5sh (3.67), 319.5 (3.38), 333 (3.44); NMR ($CDCl_3$): 1.31 (d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.62 and 1.75 (each bs, $-CH=C(C\underline{H}_3)_2$), 2.36 (s, $C_3-C\underline{H}_3$), 5.20 (overlap, $-O\underline{H}$, exchanged with $D_2O$), 5.32 (bt, J=7 Hz, $-C\underline{H}=C(CH_3)_2$), 6.90 (s, $C_1-\underline{H}$), 7.23 (dd, J=8.5 and 2 Hz, $C_6-\underline{H}$), 7.40 (bs, $C_8-\underline{H}$), 7.87 (d, J=8.5 Hz, $C_5-\underline{H}$), which was spontaneously oxidized to an α-diketone derivative (XVIII); IR: 1657, 1605 $cm^{-1}$; NMR: 1.30 (d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.63 and 1.72 (each bs, $-CH=C(C\underline{H}_3)_2$), 2.03 (s, $C_3-C\underline{H}_3$), 5.22 (bt, J=7 Hz, $-C\underline{H}=C(CH_3)_2$), 7.39 (bs, $C_5-\underline{H}$ and $C_6-\underline{H}$), 7.86 (bs, $C_8-\underline{H}$). The presence of a methyl group at the C-3 position in IX was supported by its chemical shift (δ 2.32 in $CCl_4$), because that at the α-position (C-1 or C-4) might be expected to appear at δ ca. 2.6.[10] Further, the NMR spectrum of IX in pyridine-$d_5$ showed two singlets at δ 2.66 and 7.46 due to the methyl group and an aromatic proton. These pyridine-induced solvent shifts[11] (Δ: - 0.30 and - 0.56 ppm) also supported the presence of a hydroxyl group at the C-2 position. The β-naphthol (IX) was then converted to the corresponding acetate (XIX); IR: 1753 $cm^{-1}$; NMR: 2.27 (s, $C_3-C\underline{H}_3$), 2.31 (s, $-OCOC\underline{H}_3$), 7.22 (s, $C_1-\underline{H}$), and the methyl ether (XX);[12] NMR: 1.31 (d, J=7 Hz, $-CH(C\underline{H}_3)_2$), 1.58 and 1.70 (each bs, $-CH=C(C\underline{H}_3)_2$), 2.30 (s, $C_3-C\underline{H}_3$), 3.87 (s, $-OC\underline{H}_3$), 5.25 (bt, J=7 Hz, $-C\underline{H}=C(CH_3)_2$), 6.80 (s, $C_1-\underline{H}$), 7.10 (dd, J=8.5 and 2 Hz, $C_6-\underline{H}$), 7.37 (bs, $C_8-\underline{H}$), 7.75 (d, J=8.5 Hz, $C_5-\underline{H}$).

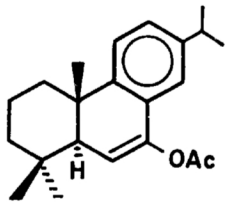
It is noteworthy that V undergoes a new type of the fragmentation reaction to the β-naphthol derivative, in contrast with Cambie's[1,2] and Tahara's[3] works which lead to the α-naphthol derivatives.



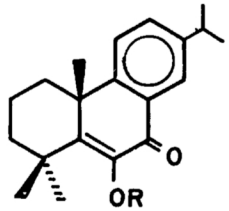
X



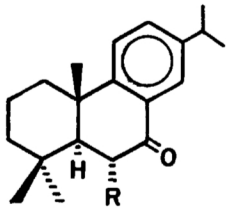
XI



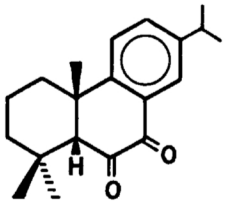
XII



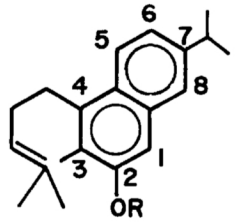
XIV R=H
XVII R=Ac



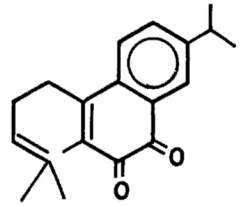
V R=OH
XIII R=Cl
XV R=OAc



XVI

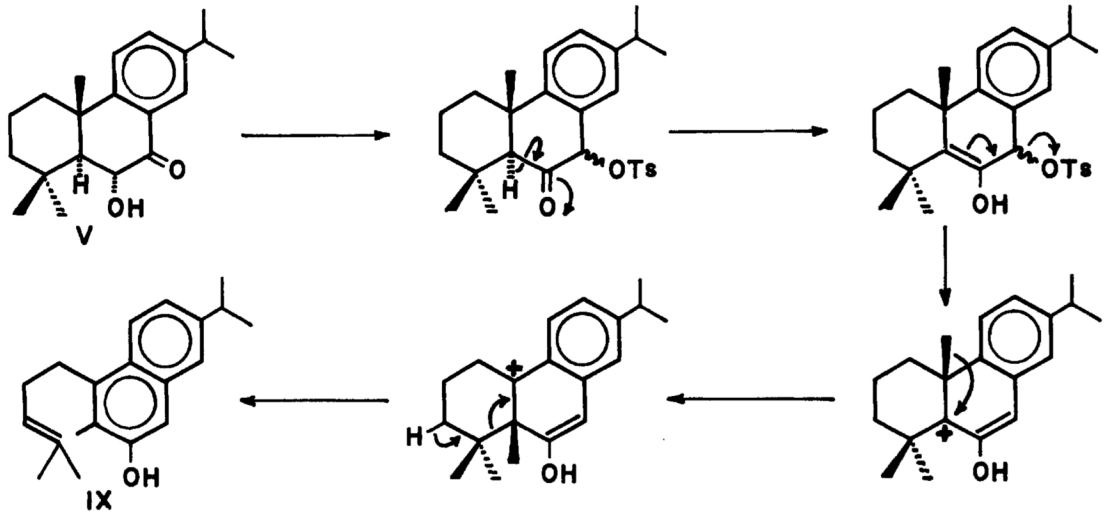


IX R=H
XIX R=Ac
XX R=Me



XVIII

A probable reaction path for transformation of V to IX is shown in the following scheme.

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IR spectra were taken in $CHCl_3$ and NMR spectra in $CCl_4$ at 60 MHz unless otherwise specified. Their chemical shifts are presented in terms of δ values.

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