

SENSITIZED PHOTOOXIDATION OF THUJOPSENOL: BIOGENETIC TYPE SYNTHESIS OF MAYURONE

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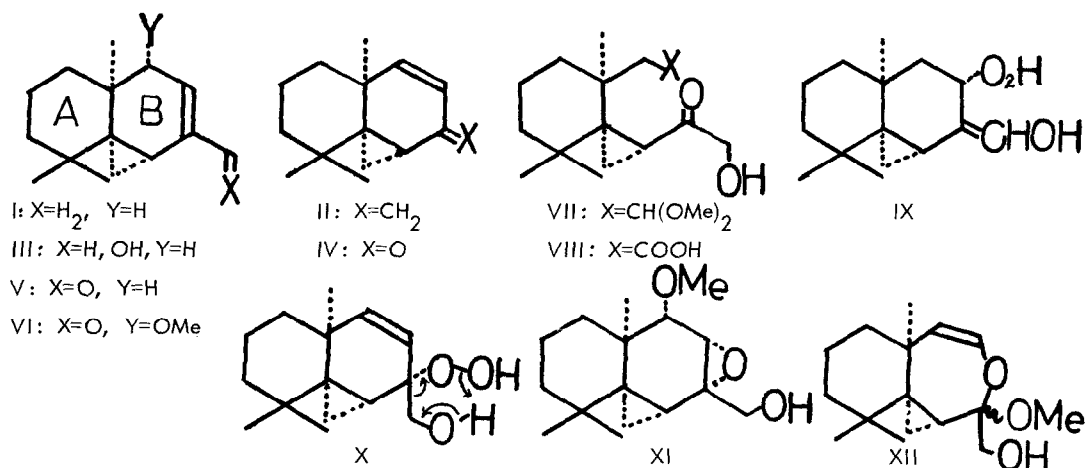
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In the previous paper (1), we described the sensitized photooxidation of thujopsene (I), which afforded, among other products, thujopsadiene (II), a sesquiterpene hydrocarbon recently isolated from Biota orientalis (2). This paper deals with the similar oxidation of thujopsenol (III) (3), which afforded mayurone (IV), a norsesquiterpenic ketone isolated from several conifers (4).

Irradiation of a methanolic solution of III with a 350 watt tungsten lamp under oxygen atmosphere in the presence of methylene blue as a sensitizer afforded several oxidation products after reductive decomposition of hydroperoxide (5). The mixture was separated by silica gel column and preparative thin layer chromatography to give five products (IV, V, VI, VII, VIII). Mayurone (IV) 15% yield (4b) Thujopsenal (V) 13% yield [δ 0.71 (3H, s), 1.13 (3H, s), 1.23 (3H, s), 5.43 (1H, dd, $J=6.5, 3.5, 2.0$), 9.44 (1H, s)] (3,6). The methoxyaldehyde (VI), colorless oil, 5% yield [ν 2830, 2740 cm^{-1} , δ 0.67 (3H, s), 1.11 (3H, s), 1.31 (3H, s), 3.24 (1H, d, $J=6.0$), 3.35 (3H, s), 6.63 (1H, br. d, $J=6.0$), 9.51 (1H, s)]. The hydroxyketoaldehyde dimethyl acetal (VII), colorless liquid, 28% yield [ν 3480, 1700 cm^{-1} , δ 0.71 (3H, s), 1.00 (3H, s), 1.22 (3H, s), 3.23 (3H, s), 3.30 (3H, s), 3.73 (1H, s, OH), 4.44 (2H, s)] and the hydroxyketocarboxylic acid (VIII), m.p. 187-8°, 5% yield [ν 3500-2700, 1730-1685 cm^{-1} , δ 0.73 (3H, s), 1.10 (3H, s), 1.20 (3H, s), 1.83 and 3.00 (AB, $J=12.5$), 4.40 (2H, s)] (7).

The structure of VI was established as follows. By reduction with zinc in acetic acid, VI was converted to III, revealing the carbon skeleton. An axial conformation of the methoxyl group was suggested from the large coupling constant ($J=6.0$) of the olefinic proton (8). Assuming a half boat conformation for ring B in VI and III (J_s for the olefinic proton are 6.0 and 3.5) as in the case of I (1,9), the axial orientation of the methoxyl group means α -configuration.

The main features of the photooxidation can be explained by a mechanism similar to that proposed for I (1). In the present case, however, the secondary allylic hydroperoxide (IX), formed by abstraction of one of the hydrogens of the hydroxymethylene, is a β -hydroperoxylaldehyde which eliminates hydrogen peroxide to give V during or after the photooxidation. Similarly, the tertiary allylic hydroperoxide formed by abstraction of a ring hydrogen is the hydroxy-hydroperoxide (X) which decomposes with the



elimination of formaldehyde (see arrows) to give IV. The formation of VI and VII would involve XI and XII (or their equivalents), respectively, as intermediates after formation of X. VIII can be formed from VII because VII was converted to VIII on standing in air.

The ratio of the yield of the product, V/IV+VI+VII+VIII (=IX/X), is ca 1/4, suggesting the half-boat conformation of ring B in III as in I (1).

For the biogenesis of IV, Chetty and Dev (4a) suggested a pathway which was actually carried out earlier by Nozoe et al (10). In view of the mildness of the reaction condition, however, the sensitized photooxidation, we believe, is the more likely process in nature.

References and Footnotes

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- 5) Thuajopsenol is stable in dark toward oxygen.
- 6) All compounds described shows correct analytical figures for the formulation. IR spectra were taken for KBr disk or CCl₄ solution. NMR spectra were measured for CCl₄ solution. Chemical shifts (δ) were expressed in ppm from internal TMS and coupling constants (J) in Hz.
- 7) This compound was obtained as an abnormal ozonization product of I. Unpublished data by T. Nozoe, H. Takeshita and H. Akiyama.
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