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Photochemical Reaction of Friedelin. Formation of an ε,ζ-Unsaturated Aldehyde

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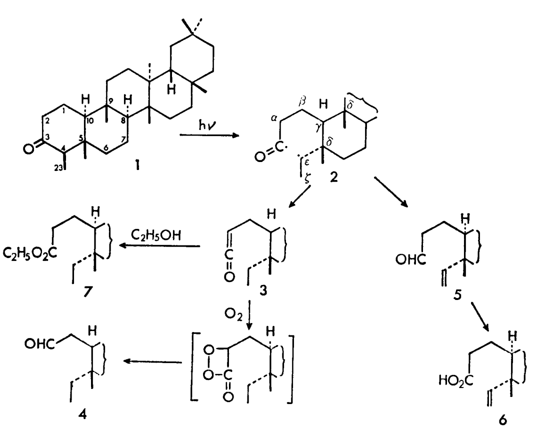
Synopsis. Friedelin (**1**) in *n*-pentane or ethanol was irradiated using a high pressure mercury lamp under a nitrogen atmosphere. From the aldehydic fraction of the photolysate, an ε,ζ-unsaturated aldehyde, 10β-(2-formylethyl)-5α-vinyl-des-*A*-friedelane (**5**) has been isolated. Upon oxidation with silver oxide, **5** afforded putranjivic acid (**6**).

Previously we reported the formation of the seco-nor saturated aldehyde (**4**), an autoxidation product of the ketene (**3**) which was formed by photoreaction of friedelin (**1**) in aprotic solvents, together with the mechanistic elucidation of the formation of **4**.[1] Attention was drawn to the fact that since there is no hydrogen atom on the δ-carbon atoms in the seco-friedelin skeleton (**2**), the usual formation of a δ,ε-unsaturated aldehyde by α-cleavage, followed by transfer of the δ-hydrogen atom through a six-membered transition state, is not feasible.

In this paper we wish to describe the formation of an ε,ζ-unsaturated aldehyde on the photolysis of friedelin (**1**). An aldehydic fraction of the photolysate of friedelin (**1**) in *n*-pentane or ethanol was reinvestigated and an unsaturated aldehyde was isolated in 2 and 0.4% yields, respectively. The unsaturated aldehyde (**5**), mp 133.5—135 °C, $[\alpha]_D$ +10° ($CHCl_3$), had a molecular formula $C_{30}H_{50}O$, determined by high resolution mass spectrometry. The PMR and IR spectra showed the presence of the groupings $-CH_2CHO$ and $-CH{=}CH_2$ (*cf.* Experimental). These data suggested that the unsaturated aldehyde (**5**) should be 10β-(2-formylethyl)-5α-vinyl-des-*A*-friedelane. This was confirmed by oxidation of **5** with silver oxide to give putranjivic acid (**6**).[2]

The formation of ε,ζ-unsaturated aldehydes is not frequently encountered.[3—5] It seems to be more likely that the ε,ζ-unsaturated aldehyde (**5**) was produced by intramolecular transfer of a hydrogen atom from a ζ-carbon atom (C-23) to the acyl radical through an eight-membered transition state,[3] rather than by intermolecular mechanisms with solvent participation. In the case of ethanol as a solvent, it would be expected that the acylalkyl biradical (**2**) undergoes a preferential hydrogen transfer reaction from C-2 to the alkyl radical through a six-membered transition state to yield the ketene (**3**), which is immediately stabilized by the reaction with ethanol yielding a seco-ester (**7**). It is therefore suggested that the acylalkyl biradical (**2**) in such circumstances undergoes a hydrogen transfer reaction *via* the eight-membered transition state to give the ε,ζ-unsaturated aldehyde (**5**).



Experimental

IR spectra were measured on a Hitachi EPI-G2 spectrometer. Mass spectra were taken on a Hitachi RMU-6-Tokugata mass spectrometer operating at 70 eV with a direct inlet system. High resolution mass spectra were taken using a Hitachi RMH-2 mass spectrometer at 70 eV. PMR spectra were measured using a Hitachi R-24 (60 MHz) spectrometer. Chemical shifts were expressed in ppm downfield from TMS as an internal standard and coupling constants in Hz. Optical rotation was measured with a JASCO DIP-SL polarimeter. Melting points were determined using a Mel-temp (Laboratory Devices) and are reported uncorrected.

Photolysis of Friedelin (1). *In* n-*Pentane*: A solution of friedelin (**1**; 1.05 g) in *n*-pentane (850 ml) was irradiated with a high pressure mercury lamp (100 W) under a nitrogen atmosphere for 9 hr at room temperature. After the irradiation, dry oxygen was passed through the solution in the dark for 14 hr at room temperature.

A part (250 ml) of the solution, on evaporation of the solvent under reduced pressure, afforded a residue (346 mg), which was separated on a silica gel (300 g) column and eluted with the following solvents (each fraction 200 ml): frs 1—7, light petroleum; frs 8—10, light petroleum–benzene (10:1); frs 11—16, light petroleum–benzene (5:1); frs 17—35, light petroleum–benzene (3:1). From fractions 27 and 28, the seco-nor aldehyde (**4**; 9 mg) was obtained and was shown to be identical with an authentic specimen.[1] Fractions 31 to 34, on evaporation, gave white crystals (6 mg; 2% yield from **1**). Mp 133.5—135 °C (from light petroleum); $[\alpha]_D$ +10° (*c*, 0.78; $CHCl_3$); MW (by high resolution mass spectrometry) 426.3887. Calcd for $C_{30}H_{50}O$: 426.3859; IR (Nujol) 2700, 1725, 1630, 1005, and 910 cm^{-1}; PMR ($CDCl_3$) δ 2.15—2.60 (2H, m, $-C\underline{H}_2-CHO$), ABX type signals due to vinyl protons $\left[{}_{H_X}\!\!>\!C{=}C\!<\!{}^{H_A}_{H_B}\right]$ δ_A 4.92 (J_{AX}=18 Hz, J_{AB}=1.6 Hz), δ_B 4.96 (J_{BX}=10 Hz, J_{AB}=1.6 Hz), and δ_X 5.71 (J_{AX}=18 Hz, J_{BX}=10 Hz)], and δ 9.65 (1H, t, *J*=2.5 Hz,

-CH_2-$C\underline{H}O$); Mass *m/e* 426 (M^+, 8%*), *m/e* 411 [$(M-15)^+$, 12%], *m/e* 301 [$(M-C_8H_{13}O)^+$, a fragment ion due to fissions of C_5-C_6 and C_9-C_{10}, 8%], *m/e* 273 (24%), *m/e* 218 (32%), 205 (90%), and 109 (100%).

In Ethanol: Friedelin (**1**; 500 mg) in ethanol (750 ml) was irradiated for 30 hr by the same procedure as above. The reaction products, after removal of the solvent, were chromatographed on a silica gel column. The ethyl ester (**7**) was eluted with light petroleum–benzene (5:1) (66% yield from **1**) and then the unsaturated seco aldehyde (**5**; 0.4% yield from **1**) was eluted with the same eluent. This was purified by repetitive chromatography on silica gel.

Oxidation of 10β-(2-Formylethyl)-5α-vinyl-des-A-friedelane (5). To a solution of the unsaturated aldehyde (**5**; 25 mg) in ethanol (10 ml), silver nitrate (50 mg) in water (1 ml) and 0.05 M sodium hydroxide solution (20 ml) were added in turn, and the reaction mixture was stirred overnight. Usual work-up and extraction with ether afforded a residue, which was chromatographed on silica gel (50 g) and eluted with benzene-ether (10:1, each fraction 30 ml). Fractions 7 and 8, on evaporation of the solvents, afforded 8 mg (31% yield from **5**) of crystals, which was identified by direct comparison (IR, tlc (SiO_2-$AgNO_3$), and Mass) with the authentic putranjivic acid (**6**), prepared by the photoxidation of friedelin (**1**).[2e)] MW (by high resolution mass spectrometry) 442.3816. Calcd for $C_{30}H_{50}O_2$: 442.3808.

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* Relative intensities of peaks above *m/e* 100.

References

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