An Unusual Photochemical Reaction of Friedelin

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The photochemical reaction of friedelin has already been reported.[1-3] We now wish to describe a photochemical cleavage of friedelin to form an unusual product whose formation is not known.

Photochemical Cleavage of Friedelin in *n*-Hexane. The suspension of friedelin (I, 1.00 g) in *n*-hexane (500 g) was heated under reflux with bubbling of argon for 1 hr. The solution was then irradiated with a high pressure mercury lamp (100 W) under an argon atmosphere for 8 hr at room temperature. After the solvent was distilled off under reduced pressure, the products were separated to hydrocarbon, aldehyde, ketene, ketone and carboxylic acid with silica gel chromatography.

From TLC examination (SiO_2; PhH:Et_2O, 10 : 1), the carboxylic acid was shown to be a mixture of two components. One of the components, with a lower R_f value, was identical with 3,4-secofriedelan-3-oic acid (II, R=H),[1,2] and the other was an unknown carboxylic acid.

After the ketene fraction was dissolved in benzene and heated with water for 2 hr, the same mixture was obtained as an acid fraction. The carboxylic acids were then esterified with diazomethane and separated to methyl 3,4-secofriedelan-3-oate (II, R=Me, 135 mg) and the other methyl ester (105 mg, about 10 per cent based on I). On mass spectra, the molecular ion peak of the latter appeared at *m*/*e* 444, which was 14 mass units (due to CH_2) lower than that of II(R=Me). Moreover, the peaks of $(M-56)^+$ were seen in the spectra of the two methyl esters. A loss of 56 mass units could be interpreted by the fragmentation 'a' (Fig. 1).

From these facts, the latter ester was inferred to be 5α-ethyl-10β-carbomethoxymethyl-des-A-friedelane (III, R=Me). This material was identical (mp, GLC, IR, mass and NMR spectra) with the authentic sample, obtained by the following method (Barbier-Wieland degradation) from ethyl 3,4-secofriedelan-3-oate (II, R=Et).

Synthesis of 5α-Ethyl-10β-carbomethoxymethyl-des-A-friedelane (III, R=Me). Irradiation of friedelin in ethanol gave ethyl 3,4-secofriedelan-3-oate (II, R=Et),[2] which afforded 3,3-diphenyl-3,4-secofriedelan-3-ol (IV) [mp 189—190°C, ν_{O-H} 3560 cm^{-1}, $C_{42}H_{62}O$] on Grignard reaction with phenylmagnesium bromide in tetrahydrofuran. IV gave 3,3-diphenyl-3,4-secofriedel-2-ene (V) [mp 202—203°C, $C_{42}H_{60}$] by dehydration with iodine and benzene. On oxidation of V with acetic acid and chromium trioxide, 5α-ethyl-10β-carboxymethyl-des-A-friedelane (III, R=H) [mp 249—250°C, $\nu_{C=O}$ 1695 cm^{-1}, $C_{29}H_{52}O_2$] was obtained. III(R=H) was esterified with diazomethane to give 5α-ethyl-10β-carbomethoxymethyl-des-A-friedelane (III, R=Me) [mp 173—174°C, $\nu_{C=O}$ 1735 cm^{-1}, mw 444 (mass). Found: C, 81.27; H, 11.81%. Calcd for $C_{30}H_{52}O_2$: C, 81.02; H, 11.79%].

Thus the unknown carboxylic acid was confirmed to be 5α-ethyl-10β-carboxymethyl-des-A-friedelane (III, R=H). This type of photochemical process giving rise to III(R=H) has never been reported. Studies to clarify this process are under way.

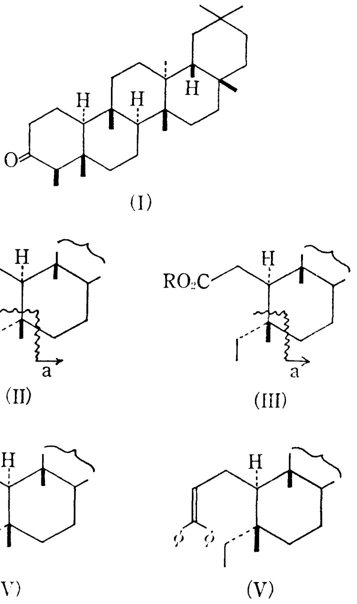

Fig. 1

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[3] T. Tsuyuki, R. Aoyagi, S. Yamada and T. Takahashi, *Tetrahedron Lett.*, **1968**, 5263.