Mechanism of Photochemical Reaction of Friedelin with Diethyl Ether and with Acetone[1)]

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Photo-irradiation of friedelin (**1**) in diethyl ether gave a keto ether (**2**), a hydroxy ether (**3**), and an alcohol (**4**). A hydroxy ketone (**5**) was formed by the photo-irradiation reaction of **1** in diethyl ether containing acetone. In the latter case, labeled experiments showed that the photo-produced ketene (**12**) reacted with 1-hydroxy-1-methylethyl radical derived from acetone to give **5**. The formation of **2** could be explained by an attack of an α-radical derived from diethyl ether to **12**. Both **3** and **4** were shown to be derived from a norseco-aldehyde (**11**) which was produced from the ketene (**12**).

The photochemical reaction of friedelin (**1**) in various organic solvents has been reported.[2)] In the present communication, the formation of a keto ether (**2**), a hydroxy ether (**3**), and an alcohol (**4**) by photo-irradiation of **1** in diethyl ether is described. The isolation of a hydroxy ketone (**5**) from the photolysate of **1** in diethyl ether containing acetone is also reported.

Friedelin (**1**) was irradiated in anhydrous diethyl ether under nitrogen* with a high pressure mercury lamp (100 W) for 7 h at room temperature. After the usual work-up, the reaction product proved to be a complex mixture which showed on a thin layer chromatogram (silica gel) three major spots (A, B, and C) and three minor spots in addition to those attributable to known hydrocarbons,[2a,d)] aldehydes,[2f,g,i)] friedelin, and 4-epifriedelin.[2c)] The fraction A gave a keto ether component (**2**). Three diastereomers of hydroxy ether (**3a**—**c**) were obtained from the fractions A, B, and C. From the fraction C, an alcohol (**4**) was obtained.

The keto ether component (**2**) had a molecular formula $C_{31}H_{60}O_2$, which corresponds to a 1 : 1 addition product of friedelin (**1**) and diethyl ether. The IR spectrum showed a carbonyl absorption. In the PMR spectrum, the presence of an α′-methylene group and an α-methine group to an ether oxygen atom was detected. The presence of the ether-moiety was further substantiated by a peak at *m/e* 427 due to a fragmentation $(M-CH_3CH_2OCHCH_3)^+$.

Although the keto ether component (**2**) is considered to consist of a mixture of diastereomers, no information on this point was obtained from its spectral data and a separation of diastereomers by thin layer chromatography using various developing solvents was unsuccessful.

The proposed structure was supported by the following chemical transformations. The reduction of the keto ether (**2**) with lithium aluminium hydride afforded a mixture of hydroxy ethers (**6**). The ether linkage of **6** was cleaved by treatment with boron trichloride[3)] to give a mixture of diols (**7**), which on oxidation with lead tetraacetate afforded an aldehyde (**8**). This aldehyde was found to be identical with the seco-aldehyde (**8**) prepared by oxidation of the known seco-alcohol (**9**)[2d)] (Scheme 1). From these observations, the keto ether (**2**) was formulated as 10β-(4-ethoxy-3-oxopentyl)-5α-ethyl-des-A-friedelane.

Three stereoisomeric hydroxy ethers (**3a**—**c**) from the fractions A, B, and C gave similar spectral data. The IR spectrum and mass spectrum (a peak at *m/e* 414 due to a fragment ion $(M-CH_3CH_2OCH_2CH_3)^+$) of each hydroxy ether (**3a**—**c**) showed the presence of a hydroxyl group and an ether-moiety. The high resolution mass spectrum showed a formula $C_{33}H_{60}O_2$ for **3**. In the PMR spectrum of **3b**, an α′-methylene and α-methine to the ether oxygen atom resonated as quartet, respectively. These results suggest that these hydroxy ethers (**3**) should be formulated as 10β-(3-ethoxy-2-hydroxybutyl)-5α-ethyl-des-A-friedelane.

These hydroxy ethers (**3a**—**c**) were combined and were treated with boron trichloride[3)] to afford a mixture of diols (**10**), which was then oxidized with lead tetraacetate to give a known norseco-aldehyde (**11**)[2f,g,j)] (Scheme 1). The structure of **3** thus determined has two additional asymmetric carbon atoms in addition to those present in 3,4-seco-friedelane skeleton. Although four diastereomers should be obtained theoretically, only three isomers could be isolated from the photolysate. A question, however, whether one of them consists of a mixture of two diastereomers remains to be proved. Configurations have not been assigned to these diastereomers.

The alcohol (**4**) was identical with 5α-ethyl-10β-(2-hydroxyethyl)-des-A-friedelane[2j)] obtained by reduction of the known norseco-aldehyde (**11**).[2f,g,j)]

The oxidation state of the isolated norseco-products, corresponding to an overall reduction, was rather unexpected and requires an explanation. Since the norseco-alcohol (**4**) obtained from irradiation of friedelin-^{18}O (**1**-^{18}O; isotopic abundance, *ca.* 17%)[2g,j)] was shown to contain no ^{18}O atom, the oxygen atom in **4** is not derived from the oxygen atom of the friedelin carbonyl group. The experimental data is shown in Table 1.

We have previously shown[2g,j)] that the ketene (**12**), formed by irradiation of friedelin (**1**) *via* an acyl-alkyl biradical (**13**), is autoxidized with oxygen during the product isolation to afford the norseco-aldehyde (**11**). Two mechanisms have now been considered for the formation of **4**: (i) a mechanism involving a carbene (**14**)[4)] and (ii) a mechanism *via* the norseco-aldehyde (**11**).

In terms of mechanism (i), the ketene (**12**) might

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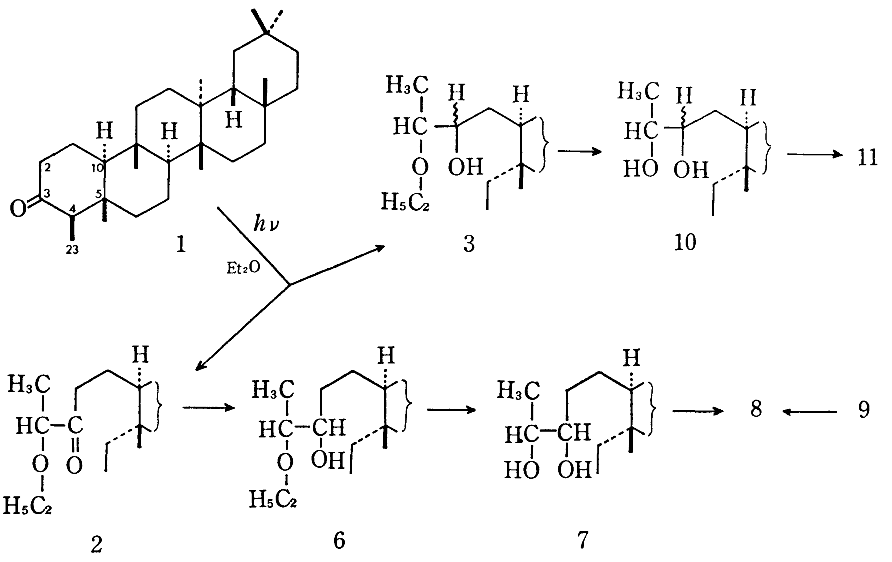
* The commercial nitrogen was used without purification.



Scheme 1.

TABLE 1. ^{18}O-ISOTOPIC ABUNDANCE[a] IN **4** (FROM **1**-^{18}O) AND RELATED COMPOUNDS

	m/e 426	m/e 427	m/e 428
1 (M^+, m/e 426)	100	34.6	6.4
1-^{18}O	100	33.7	23.7
	m/e 416	m/e 417	m/e 418
4 (M^+, m/e 416)	100	32.3	5.8
4 (from **1**-^{18}O)	100	32.5	6.6

a) Relative intensities in %.

undergo decarbonylation on irradiation affording a carbene (**14**), which could react with water to give the norseco-alcohol (**4**) (Scheme 2).

To test this hypothesis, friedelin (**1**) was irradiated in water-free ether saturated with deuterium oxide (99.75% D_2O) and the norseco-alcohol (**4**) was isolated. If the reaction had proceeded through the carbene (**14**), the product would have been the dideuterio alcohol (**4**-d_2), which would give a monodeuterio alcohol (**4**-d_1) by usual aqueous work-up. Therefore, the reaction product should contain *one* deuterium atom at C-2 as shown in **4**-d_1.

The mass spectrometric examination of the product showed, however, that the incorporation of a deuterium atom had not occurred (Table 2) and that the mechanism (i) can consequently be excluded.

Directing attention to the second mechanism, the photo-produced ketene (**12**) could be autoxidized by oxygen[2g,j,5,6] which may be present in the reaction system to afford the norseco-aldehyde (**11**). The aldehyde (**11**) would then undergo photochemical reduction[7] in ether to give the norseco-alcohol (**4**).

TABLE 2. D-ISOTOPIC ABUNDANCE[a] IN **4**

	m/e 416	m/e 417	m/e 418
4 (authentic; M^+, m/e 416)	100	32.3	5.4
4 (photoproduct)	100	32.3	6.7
4 (photoproduct obtained by irradiation with D_2O)	100	32.1	5.7

a) Relative intensities in %.

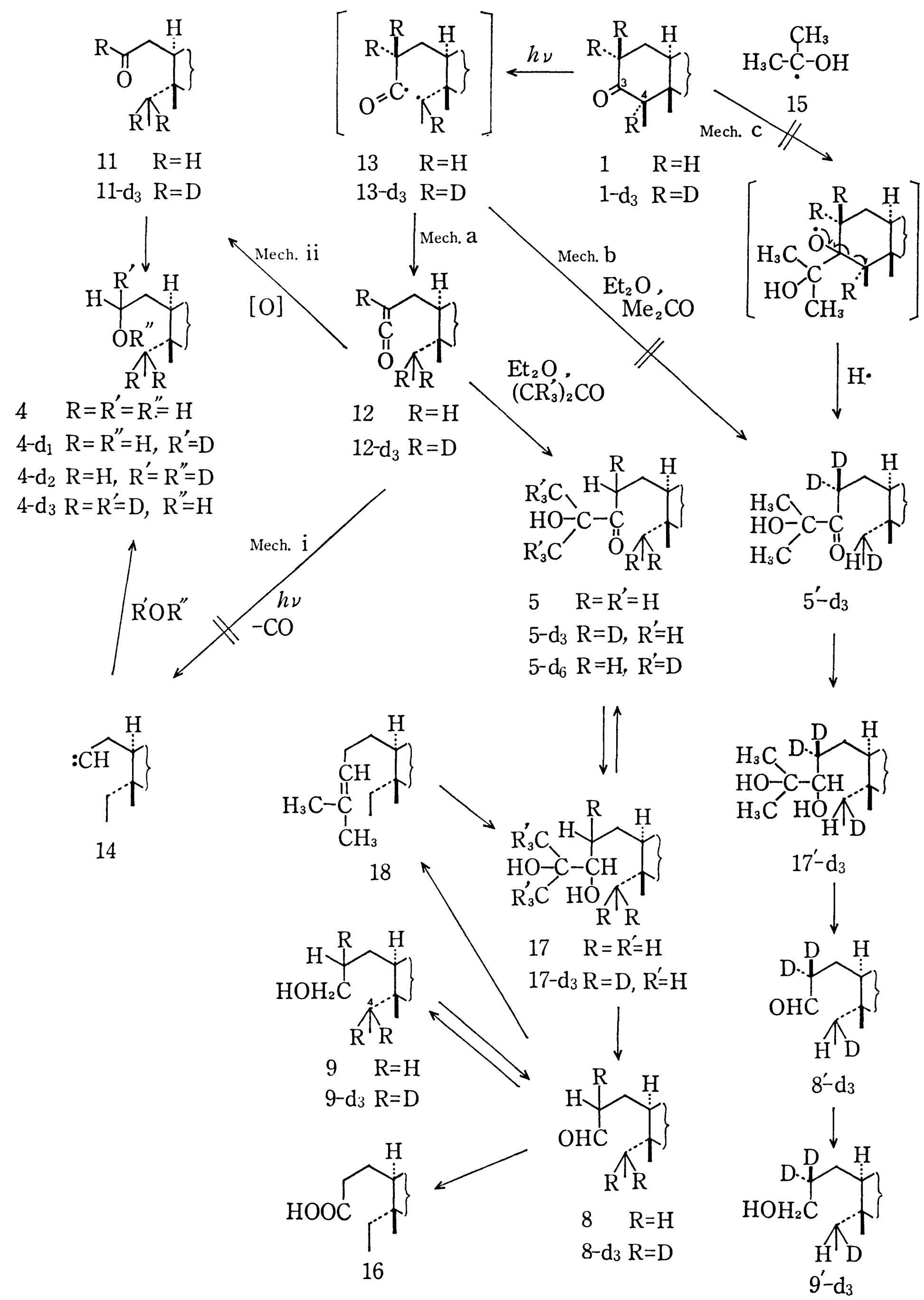
The involvement of oxygen in the formation of **4** was demonstrated as follows. Friedelin (**1**) was irradiated in anhydrous diethyl ether under oxygen-free argon purified by passing over copper at 500 °C. The hydrocarbons, aldehydes, friedelin, 4-epifriedelin, and the keto ether (**2**) were obtained, while neither the hydroxy ether (**3**) nor the norseco-alcohol (**4**) was detected by thin layer chromatography. Since the irradiation of friedelin (**1**) under commercial nitrogen gave **3** and **4**, oxygen present in the commercial nitrogen is implicated in the formation of these products. Following this conclusion, the intermediacy of the ketene (**12**) and norseco-aldehyde (**11**) in the photo-reaction was examined.

Irradiation of 2α,2β,4α-trideuteriofriedelin (**1**-d_3)[2g,i] in ether afforded a deuteriated alcohol (**4**-d_3), which gave a molecular ion peak at m/e 419. The methylene group at C-2 in **4** resonated as a triplet with an integrated intensity due to two protons, while the integrated intensity of a triplet in **4**-d_3 corresponded to one proton. On addition of $Eu(dpm)_3$ as a shift reagent, the C-4 methyl protons were readily assignable with the triplet signal for nonlabeled alcohol (**4**) appearing as a singlet in **4**-d_3. These observations indicate that the methylene group at C-4 of **4**-d_3 was labeled with two deuterium atoms and the methylene group at C-2 with one deuterium atom, in accordance with formation of **4**-d_3 *via* the ketene (**12**-d_3).

The norseco-aldehyde (**11**)[2f,j] was irradiated in ether, and from the reaction products, the norseco-alcohol (**4**) and the hydroxy ether (**3**) were isolated.

These experimental results show that the ketene (**12**) formed by irradiation is autoxidized with oxygen in the reaction system to give the norseco-aldehyde (**11**), which is subsequently reduced photochemically to yield **3** and **4**. The final photoreduction step[7] is outlined in Scheme 3.

The formation of the keto ether (**2**) is likely to suggest a novel reaction between a photochemically produced ketene and an α-radical derived from diethyl ether.



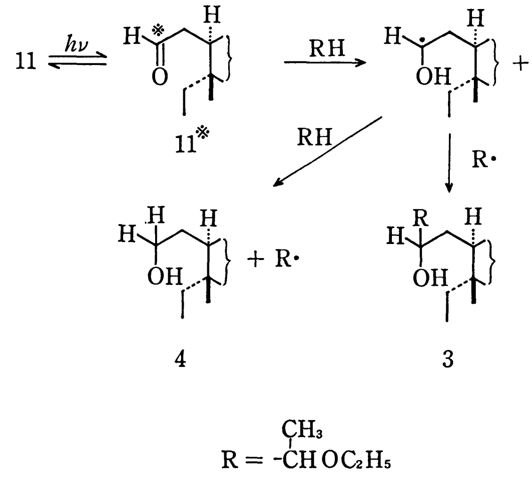
Scheme 2.

Friedelin (**1**) in ether containing acetone was irradiated in a quartz vessel under the usual conditions. The irradiation products were separated by column and thin layer chromatography to give a hydroxy ketone (**5**), whose PMR spectrum showed the presence of $(CH_3)_2C$-(OH)- group and whose molecular formula $C_{33}H_{58}O_2$ showed an increment of C_3H_8O in comparison with that of friedelin. On acetylation, the hydroxy ketone (**5**) gave an acetoxy ketone.

The structure of the hydroxy ketone (**5**) was confirmed by conversion to the known 10β-(2-carboxyethyl)-5α-ethyl-des-A-friedelane (**16**).[2b] It was subjected to consecutive reduction with lithium aluminium hydride, oxidation with lead tetraacetate and with silver oxide to afford a seco-acid (**16**) (Scheme 2).

A partial synthesis of **5** confirmed the proposed structure. The aldehyde (**8**) was treated with isopropyltriphenylphosphonium bromide.[8,9] The resulting isopropylidene derivative (**18**)[10] was oxidized with osmium tetraoxide[11] to give a mixture of diols (**17**), which on oxidation with chromium trioxide[12] yielded the hydroxy ketone (**5**), identical with the photo-irradiation product (Scheme 2).

A solution of **1** in ether and acetone-d_6 was irradiated for 5 h, and the resulting hydroxy ketone (**5**-d_6) was isolated and examined. The molecular ion peak was observed at *m/e* 492, *i.e.* 6 mass units higher than that of the non-labeled **5**. In the PMR spectrum, a singlet



$R = -\overset{CH_3}{CH}OC_2H_5$

(An asterisk refers to an activated state.)

Scheme 3.

signal (δ 1.37) due to two tertiary methyl group in **5** was not observed in **5**-d_6. The presence of pinacol in the photolysate was demonstrated by gas chromatographic examination further supporting the involvement of 1-hydroxy-1-methylethyl radical (**15**) in the photolysis of friedelin (**1**) in ether containing acetone.

Three mechanisms (outlined in Scheme 2 as "a", "b", and "c") were considered for the formation of the hydroxy ketone (**5**). a) The attack of the radical (**15**) at the carbonyl carbon atom of the ketene (**12**), followed by addition of a hydrogen atom to C-2. b) The addition of the radical (**15**) to the acyl radical (C-3) of the biradical (**13**), followed by addition of a hydrogen atom to the alkyl radical (original C-4 of friedelin). c) The attack of the radical (**15**) to the carbonyl carbon atom (C-3) of friedelin (**1**), followed by β-scission between C-3 and C-4, and then by addition of a hydrogen atom to the carbon atom at C-4.

In order to distinguish among these hypotheses, 2α,2β,4α-trideuteriofriedelin (**1**-d_3) was irradiated in ether containing acetone. A trideuteriated hydroxy ketone (**5**-d_3) was obtained showing the molecular ion peak at *m/e* 489. The trideuteriated hydroxy ketone (**5**-d_3) was degradated to give **8**-d_3 and **9**-d_3 by the previously described procedures. In the PMR of the trideuteriated seco-aldehyde (**8**-d_3), the aldehydic proton was observed as a doublet. Furthermore, a triplet signal due to the methyl group (proton on C-23) attached to the C-4 atom of non-labeled alcohol (**9**) appeared as a singlet in the case of the trideuteriated seco-alcohol (**9**-d_3).

These observations lead to the conclusion that 1-hydroxy-1-methylethyl radical (**15**) attacked the carbonyl carbon atom of the ketene (**12**) to form a C-2 radical, which abstracts a hydrogen atom from the solvent (mechanism "a"). The alternative mechanisms "b" and "c" are excluded by the same experiment, since the degradation of the photo-product (**5'**-d_3) would lead to the aldehyde (**8'**-d_3) and then to the alcohol (**9'**-d_3). The aldehydic proton of **8'**-d_3 and the methyl protons at C-4 of **9'**-d_3 should resonate as a singlet and a doublet, respectively, in the PMR spectra. The formation of the keto ether (**2**), obtained by the photo-irradiation of friedelin (**1**) in ether, may also best be interpreted by a pathway analogous to the mechanism "a".

Experimental

Instruments and general procedures are described in previous papers.[1,2k] Gas-liquid phase chromatographic (GLC) analyses were determined on a Shimadzu gas chromatograph model GC-6A. Analytical and preparative thin layer chromatographies (TLC) were carried out on Kieselgel G nach Stahl (E. Merck) and Silica gel PF$_{254}$ (E. Merck), respectively. Column chromatography was carried out on Wakogel C-200 (Wako). Diethyl ether (Wako) was washed with dilute sulfuric acid and water and dried over calcium chloride. The ether was distilled from lithium aluminium hydride. Acetone (Wako) was dried over potassium carbonate and distilled.

Photochemical Reaction of Friedelin (1) in Diethyl Ether. Nitrogen (Suzuki-shokan Co.) was bubbled through a refluxing solution of friedelin (**1**: 455 mg) in diethyl ether (300 ml) for 30 min, then the solution cooled to room temperature was irradiated with a high pressure mercury lamp for 7 h under nitrogen. The solvent was evaporated under reduced pressure, the residue dissolved in benzene and passed through a column of silica gel (50 g), and eluted with benzene (each fraction 50 ml). In fractions 1—3, hydrocarbons and aldehydes were eluted and from fractions 4—13 a residue (131 mg) was obtained. Subjection of the residue to preparative TLC using benzene–chloroform (1: 1) afforded fractions A, B, and C. Each fraction was further separated by preparative TLC developed with benzene–ether (10: 1).

The keto ether (**2**; 24 mg) was isolated from the fraction A but could not be separated into each diastereomer by TLC using various eluents. A few milli grams of a stereoisomer of the hydroxy ether (**3a**; IR (Nujol) 3580, 3470, and 1100 cm^{-1}; MS *m/e* 488) was also obtained from the fraction A.

The fraction B gave a diastereomer of the hydroxy ether (**3b**; about 40 mg) by the second preparative TLC, IR (Nujol) 3580, 3470, and 1100 cm^{-1}; MS *m/e* 488; the PMR and high resolution mass spectra (*vide infra*).

From the fraction C, the third isomer of the hydroxy ether (**3c**; a few mg; IR (Nujol) 3580, 3470, and 1100 cm^{-1}; MS *m/e* 488) and the norseco-alcohol (**4**; 9 mg) were isolated.

10β-(4-Ethoxy-3-oxopentyl)-5α-ethyl-des-A-friedelane (2). The keto ether (**2**) was obtained as an oil, IR (Nujol) 1705, 1110, 1000, 910, 850, and 800 cm^{-1}; PMR δ ≈0.80 (6H, s and t overlapped, 2×CH$_3$), 0.89, 0.97, 1.20, 1.25 (each 3H, s, *t*-CH$_3$), 1.00—1.05 (12H, br. s, 4×CH$_3$), 2.58 (2H, t, J=8 Hz, $C_{(2)}$-H), 3.49 (2H, q, J=7 Hz, $CH_3C\underline{H}_2O$), and 3.79 (1H, q, J=7 Hz, $CH_3C\underline{H}$-O); MS *m/e* 500 (M$^+$, 18%), 485, 471, 455, 427, 371, 333, 312, 301, 273 (100%), 259, 245, 231, 218, and 205; Found: C, 81.24; H, 11.93%. Calcd for $C_{34}H_{60}O_2$: C, 81.53; H, 12.08%.

10β-(3-Ethoxy-2-hydroxybutyl)-5α-ethyl-des-A-friedelane (3). Three diastereomers (**3a**—**c**) were obtained as oil and gave similar spectral data (*vide supra*). The hydroxy ether (**3b**), obtained from fraction B, provided the following data; IR (Nujol) 3580, 3470, 1100, 1000, 850, and 800 cm^{-1}; PMR δ ≈0.80 (6H, s and t overlapped, 2×CH$_3$), 0.90, 0.96 (each 3H, s, *t*-CH$_3$), 1.01 (12H, br. s, 4×CH$_3$), 1.19 (6H, s, 2×CH$_3$), 3.48 (2H, q, J=7 Hz, $CH_3C\underline{H}_2O$), 3.52 (1H, q, J=7 Hz, $CH_3C\underline{H}$-O), and 3.3—3.8 (1H, br. s, $C_{(2)}$-H); MS *m/e* 488 (M$^+$, 22%), 473, 459, 432, 411, 402, 387, 385, 301, 273 (100%), 218, and 205; MW 488.4636 (by high resolution mass spectrometry). Calcd for $C_{33}H_{60}O_2$: 488.4591.

5α-Ethyl-10β-(2-hydroxyethyl)-des-A-friedelane (4). Crystallization from ether gave colorless crystals, mp 155—156 °C; IR (Nujol) 3300, 1050, and 800 cm^{-1}; PMR δ ≈0.80

(6H, s, and t overlapped, $2\times CH_3$), 0.89, 0.97, 1.19 (each 3H, s, *t*-CH_3), 1.01 (9H, s, $3\times$*t*-CH_3), and 3.53 (2H, t, $J=8$ Hz, $C_{(2)}$–H); MS *m/e* 416 (M^+, 33%), 401, 387, 381, 360, 301, 273 (100%), 249, 218, and 205. This was identical with an authentic 5α-ethyl-10β-(2-hydroxyethyl)-des-A-friedelane (**4**).

Degradation of 10β-(4-Ethoxy-3-oxopentyl)-5α-ethyl-des-A-friedelane (2). The keto ether (**2**; 38 mg) in ether (30 ml) and lithium aluminium hydride (150 mg) were heated under reflux for 3 h. The usual work-up and separation on preparative TLC using benzene–ether (10: 1) gave 10β-(4-ethoxy-3-hydroxypentyl)-5α-ethyl-des-A-friedelane (**6**; 32 mg) as a mixture of diastereomers; an amorphous solid, IR (Nujol) 3550, 3450, 1100, 1000, 840, and 800 cm^{-1}; PMR δ ≈0.79 (6H, s and t overlapped, $2\times CH_3$), 0.89, 0.95 (each 3H, s, *t*-CH_3), 1.00 (12H, br. s, $4\times CH_3$), and 3.15—3.85 (4H, m, CH–O–); MS *m/e* 502 (M^+, 10%), 487, 473, 446, 430, 415, 401, 335, 323, 301, 273 (100%), 218, and 205.

A solution of **6** (26 mg) in dry methylene dichloride (1 ml) was kept at −78 °C, and a solution of boron trichloride (3 ml) in methylene dichloride (2 ml) was added. The resulting solution was stirred at −78 °C for 2 h and then allowed to stand overnight at room temperature. The solvent was removed under reduced pressure and aqueous methanol was added. Methanol was removed under reduced pressure and the residue was extracted with ether (100 ml). Usual work-up and purification by preparative TLC developed with benzene–ether (10: 1) afforded diastereomers of 10β-(3,4-dihydroxypentyl)-5α-ethyl-des-A-friedelane (**7**; 9 mg) as an oil; IR (Nujol) 3400 and 1080 cm^{-1}; PMR δ≈0.80 (6H, s and t overlapped, $2\times CH_3$), 0.89, 0.95, 1.19 (each 3H, s, *t*-CH_3), 1.00 (12H, br. s, $4\times CH_3$), and 3.25—3.95 (2H, m); MS *m/e* 474 (M^+, 12%), 459, 457, 445, 441, 425, 418, 413, 380, 307, 301, 273 (100%), 218, and 205.

To a solution of the diastereomeric diols (**7**; 8.4 mg) in benzene (5 ml), a saturated solution of lead tetraacetate in acetic acid (10 ml) was added and the mixture was stirred at room temperature for 2 h. A saturated aqueous sodium hydrogencarbonate solution was added and the mixture was extracted with ether. The reaction products were separated by preparative TLC using benzene to afford 5α-ethyl-10β-(2-formylethyl)-des-A-friedelane (**8**; 5.4 mg). This was identical with an authentic seco-aldehyde (**8**).

Degradation of 10β-(3-Ethoxy-2-hydroxybutyl)-5α-ethyl-des-A-friedelane (3). Due to a paucity of the hydroxy ethers (**3a**—**c**), these compounds were combined and subjected to the following degradation.

A solution of the hydroxy ethers (**3a**—**c**; 41 mg) in methylene dichloride (1 ml) was kept at −78 °C and a solution of boron trichloride (3 ml) in methylene dichloride (2 ml) was added. The resulting solution was stirred at 0 °C for 1.5 h and then at room temperature for 5 h. The solvent was removed under reduced pressure and aqueous methanol (1 ml) was added. Methanol was removed under reduced pressure and the residue was extracted with ether (100 ml). After usual work-up, the reaction mixture was separated by preparative TLC using benzene–ether (10: 1) to give diastereomers of 10β-(2,3-dihydroxybutyl)-5α-ethyl-des-A-friedelane (**10**; 18 mg) as an oil; IR (Nujol) 3400, 1050, 980, 860, and 800 cm^{-1}; PMR δ≈0.83 (6H, s and t overlapped, $2\times CH_3$), 0.90, 0.95, 1.19 (each 3H, s, *t*-CH_3), 1.10 (12H, br. s, $4\times CH_3$), and 3.20—3.38 (2H, m); MS *m/e* 460 (M^+, 31%), 445, 431, 427, 404, 380, 301, 293, 273 (100%), 218, and 205.

To a solution of the diols (**10**; 18 mg) in benzene (5 ml), a saturated solution of lead tetraacetate in acetic acid (10 ml) was added. The solution was treated according to the same procedure as in the case of the diols (**7**). 5α-Ethyl-10β-formylmethyl-des-A-friedelane (**11**; 10 mg) was obtained, mp 182 °C (crystallized from ether); IR (Nujol) 2710 and 1705 cm^{-1}; PMR δ ≈0.80 (6H, s and t overlapped, $2\times CH_3$), 0.90, 0.96, 1.20 (each 3H, s, *t*-CH_3), 1.01 (9H, s, $3\times CH_3$), and 9.78 (1H, t, $J=2.5$ Hz, –CHO); MS *m/e* 414 (M^+, 27%), 399, 301, 290, 273, 218, and 205 (100%). This was identical with an authentic norseco-aldehyde (**11**).[2f,g,j]

Photochemical Reaction of Friedelin-^{18}O (1-^{18}O) in Ether. Irradiation of friedelin-^{18}O (**1**-^{18}O; 180.7 mg) in ether (200 ml) in a quartz vessel under a nitrogen atmosphere for 10 h, followed by solvent removal under reduced pressure yielded a residue, which was chromatographed on silica gel (20 g). A norseco-alcohol fraction was further subjected to preparative TLC to give 5.2 mg of **4**. The ^{18}O-isotopic abundance in the starting material (**1**-^{18}O) and the product (**4**) was examined by the mass spectrometry (Table 1).

Photochemical Reaction of Friedelin (1) in Ether Containing Deuterium Oxide. Friedelin (**1**; 322 mg) was dissolved in ether (200 ml) which was freshly distilled from lithium aluminium hydride and was saturated with deuterium oxide (D_2O 99.75%, Showa-denko Co.). The solution was irradiated for 8 h as before. The same work-up and separation procedure gave the norseco-alcohol (**4**; 9.1 mg). The deuterium isotopic abundance of the product (**4**) was examined by mass spectrometry (*Cf.* Table 2).

Photochemical Reaction of 2α,2β,4α-Trideuteriofriedelin (1-d_3) in Ether. Trideuteriofriedelin[**] (**1**-d_3; 292 mg) in ether (200 ml) was irradiated under the same conditions for 10 h and worked up as before to afford a trideuterio norseco-alcohol (**4**-d_3; 7.3 mg), PMR δ ≈0.80 (6H, s, $2\times CH_3$), 0.89, 0.95, 1.19 (each 3H, s, *t*-CH_3), 1.00 (9H, s, $3\times$*t*-CH_3), and 3.53 (1H, t, $J=8$ Hz, $C_{(2)}$–H); MS *m/e* 419 (M^+, 19%), 404, 388, 301, 273, 218, and 205 (100%). When $Eu(dpm)_3$ was added to a 1% (w/v) solution of **4**-d_3 in $CDCl_3$ [$Eu(dpm)_3$/**4**-d_3=1.1 (in molar ratio)], $C_{(4)}$–CH_3 signal appeared at δ 2.35 as a singlet. Under the same conditions, $C_{(4)}$–CH_3 of non-labeled alcohol (**4**) resonated at δ 2.35 as a triplet ($J=7$ Hz).

Photochemical Reaction of Friedelin (1) in Ether Under Oxygen-free Argon. Friedelin (**1**; 1.07 g) in ether (700 ml) was heated under reflux for 30 min with bubbling of oxygen-free argon[***] in a quartz irradiation vessel. The solution, after cooling, was irradiated for 24 h under the oxygen-free argon at room temperature. The solvent was removed under reduced pressure to give a residue, which was examined by TLC and shown to contain neither **3** nor **4**. The residue was dissolved in benzene, passed through a column of silica gel (100 g), and eluted with benzene (each fraction 100 ml). Fractions 5 and 6 were combined and further subjected to preparative TLC developed with benzene–petroleum ether–methylene dichloride (4: 3: 2) to give keto ether component (**2**; 78 mg).

Photochemical Reaction of 5α-Ethyl-10β-formylmethyl-des-A-friedelane (11). A solution of the norseco-aldehyde (**11**; 178 mg, prepared from norfriedelin[2,j]) in ether (700 ml) was irradiated in a Pyrex vessel for 62 h under a nitrogen atmosphere at room temperature. After usual treatment, preparative TLC using benzene–chloroform (1: 1) gave the three diastereomers of hydroxy ether (**3a**—**c**; total weight 49 mg) and the norseco-alcohol (**4**; 11 mg).

Photochemical Reaction of Friedelin (1) in Ether Under an Oxygen Atmosphere. Friedelin (**1**; 1.01 g) in ether (800 ml)

[**] Mass spectrometry showed that the deuteriated friedelin (**1**-d_3) consisted of -d_3 (80%), -d_2 (20%), -d_1 (0%), and -d_0 (0%).

[***] Argon was purified by passing over copper (pretreated with a flow of hydrogen at 200 °C) placed in a quartz tube and heated at 500 °C.

was irradiated in a Pyrex vessel with a high pressure mercury lamp for 48 h under an oxygen atmosphere at room temperature.[2h] The solvent was removed to afford a residue. The TLC examination showed the presence of friedelin (recovered unchanged, a major spot), the seco-carboxylic acid (**16**), a norseco-carboxylic acid[2e,j] and putranjivic acid,[2h,13] while the presence of the hydroxy ether (**3**) and the norseco-alcohol (**4**) could not be demonstrated.

*Photochemical Reaction of Friedelin (**1**) in Ether Containing Acetone.* Friedelin (**1**; 86 mg) was dissolved in ether (30 ml) containing acetone (0.5 ml) in a quartz vessel and heated under reflux for 30 h with bubbling of nitrogen. The solution was cooled and irradiated with a high pressure mercury lamp for 2 h at room temperature. A small quantity of the solution was taken out and subjected to GLC examination, which showed the formation of pinacol (R_t 7.7 min (Carbowax C-20 M, 100 °C) and 11.7 min (DGS, 100 °C)). The reaction mixture, after evaporation of the solvent under reduced pressure, was separated by preparative TLC with benzene as eluent. 5α-Ethyl-10β-(4-hydroxy-4-methyl-3-oxopentyl)-des-A-friedelane (**5**; 12 mg) was obtained after recrystallization from light petroleum, mp 180.5—181.5 °C; IR (Nujol) 3500, 1705, and 1140 cm^{-1}; PMR δ ≈0.80 (6H, s and t overlapped), 0.89, 0.95, 1.03, 1.18 (each 3H, s, t-CH_3), 1.00 (6H, s, 2×t-CH_3), 1.37 (6H, s, $(C\underline{H}_3)_2C(OH)-$), 2.40—2.75 (2H, m, $-\overset{|}{C}\underline{H}_2-C{=}O$), and 3.77 (1H, s, $-\underset{|}{\overset{|}{C}}-OH$; disappeared on addition of D_2O); (CD_3COCD_3) δ≈4.18 (1H, s, $-\underset{|}{\overset{|}{C}}-OH$; disappeared on addition of D_2O); MS m/e 486 (M^+, 10%), 471, 457, 453, 443, 430, 428, 413, 319, 307, 275, 274, 273, and 205 (100%); Found: C, 81.57; H, 12.07%. Calcd for $C_{33}H_{58}O_2$: C, 81.42; H, 12.01%.

*Acetate of 5α-Ethyl-10β-(4-hydroxy-4-methyl-3-oxopentyl)-des-A-friedelane (**5**).* A mixture of the hydroxy ketone (**5**; 32 mg), pyridine, and acetic anhydride was heated on stream bath for 10.5 h. The reaction mixture was treated as usual and the product crystallized from methanol twice to afford the acetate (21 mg), mp 159—160 °C; IR (Nujol) 1724 and 1247 cm^{-1}; PMR δ≈0.79 (6H, s and t overlapped, 2×CH_3), 0.86, 0.94, 1.01, 1.17 (each 3H, s, t-CH_3), 0.99 (6H, s, 2×t-CH_3), 1.44 (6H, s, $(C\underline{H}_3)_2C(OAc)-$), and 2.25—2.60 (2H, m, $-CH_2C{=}O$); MS m/e 528 (M^+).

*Degradation of 5α-Ethyl-10β-(4-hydroxy-4-methyl-3-oxopentyl)-des-A-friedelane (**5**).* To the hydroxy ketone (**5**; 12 mg) in ether (5 ml), lithium aluminium hydride (17 mg) in ether (5 ml) was added and the mixture was heated under reflux for 2 h. After decomposition of the excess reagent by addition of wet ether, the mixture was treated as usual. Column chromatography of the residue on silica gel (50 g) afforded a mixture of the diastereomeric diols (**17**; 9 mg), mp 188—189 °C; IR (Nujol) 3400, 1170, 1080, and 960 cm^{-1}; PMR δ ≈0.80 (6H, s and t overlapped, 2×CH_3), 0.90, 0.96, 1.03, 1.16, 1.19, 1.21 (each 3H, s, t-CH_3), 1.01 (6H, s, 2×t-CH_3), and 4.62 (1H, s, $-\underset{|}{\overset{|}{C}}-OH$; disappeared on addition of D_2O); MS m/e 488 (M^+, 15%), 473, 470, 459, 455, 441, 432, 430, 415, 321, 309, 301, 273 (100%), 218, and 205; Found: C, 79.80; H, 12.51%. Calcd for $C_{33}H_{60}O_2\cdot 1/2\,H_2O$: C, 79.62; H, 12.35%.

A saturated solution of lead tetraacetate in acetic acid (10 ml) was added to the diols (**17**; 2.8 mg) in benzene (5 ml) and the mixture was stirred for 1 h. The excess lead tetraacetate was decomposed by addition of saturated sodium hydrogencarbonate solution until the solution became alkaline and the solution was extracted with ether (500 ml). After usual work-up, the residue was chromatographed on silica gel using benzene to give an aldehyde (**8**; 2.5 mg). This was identical with an authentic seco-aldehyde (**8**).

A mixture of silver nitrate (41 mg) in water (1 ml) and 0.05 M sodium hydroxide solution (5 ml) was added to the seco-aldehyde (**8**; 1.8 mg) in ethanol (5 ml) with stirring, which was continued for 2 h. The solvents were evaporated under reduced pressure to give a residue, to which ether (100 ml) was added. The resulting solution was acidified with 1 M hydrochloric acid and extracted with ether. After usual work-up, purification of the residue by preparative TLC afforded 10β-(2-carboxyethyl)-5α-ethyl-des-A-friedelane (**16**; 1.1 mg); IR (Nujol) 1705, 1290, and 1220 cm^{-1}; MS m/e 444 (M^+, 16%), 429, 405, 401, 388, 369, 368, 320, 301, 291, 273, 218 (100%), and 205. This was identical with an authentic seco-carboxylic acid (**16**).[2b]

*Synthesis of 5α-Ethyl-10β-(4-hydroxy-4-methyl-3-oxopentyl)-des-A-friedelane (**5**) from 5α-Ethyl-10β-(3-hydroxypropyl)-des-A-friedelane (**9**).* 5α-Ethyl-10β-(3-hydroxypropyl)-des-A-friedelane (**9**; 694 mg) was dissolved in a minimum volume of methylene dichloride and a mixture of chromium trioxide (1.34 g), pyridine (840 mg), and methylene dichloride (23 ml) was added to the solution. After stirring for 15 min, the methylene dichloride solution was separated by decantation and the precipitate was washed with methylene dichloride (150 ml). The supernatant and the washings were combined and washed with 5% sodium hydrogencarbonate solution (100 ml), 5% hydrochloric acid (100 ml), and then with 5% sodium hydrogencarbonate solution (100 ml). Usual work-up gave a residue, which was recrystallized from ether to afforded the seco-aldehyde (**8**; 657 mg); mp 147—148 °C; IR (Nujol) 2720, 1720, and 1005 cm^{-1}; PMR δ ≈0.81 (6H, s and t overlapped, 2×CH_3), 0.90, 0.96, 1.19 (each 3H, s, t-CH_3), 1.01 (9H, s, 3×t-CH_3), 2.20—2.60 (2H, m, $-C\underline{H}_2-CHO$), and 9.73 (1H, t, J=2 Hz, $-CHO$); MS m/e 428 (M^+, 9%), 413, 400, 399, 385, 372, 362, 319, 304, 279, 273, 265 (100%), 218, and 205; Found: C, 84.26; H, 12.44%. Calcd for $C_{30}H_{52}O$: C, 84.04; H, 12.23%.

To a suspension of isopropyltriphenylphosphonium bromide (960 mg) in ether, 15% butyllithium solution in hexane (2.1 ml) was added with stirring under nitrogen. A deep red solution was obtained, to which a solution of the seco-aldehyde (**8**; 206 mg) in ether (10 ml) was added. The reaction mixture was stirred for 3 h and then tetrahydrofuran (50 ml) was added. The ether was removed and the remaining solution was heated under reflux for 2 h. After cooling, water (100 ml) was added to the solution and the mixture was extracted with ether (200 ml). The ethereal extract was washed with saturated aqueous sodium chloride solution, 1 M hydrochloric acid (100 ml) and then with aqueous sodium chloride solution. Usual work-up gave a residue, which was purified by column chromatography on silica gel (30 g) using petroleum ether. Recrystallization from petroleum ether gave the isopropylidene derivative (**18**; 130 mg), mp 147.5—148 °C; IR (Nujol) 1050, 1000, and 990 cm^{-1}; PMR δ≈1.50 (3H, br., $C{=}C-CH_3$), 1.68 (3H, br., $C{=}C-CH_3$), and 5.10 (1H, t, J=7 Hz, $C{=}C\underline{H}-CH_2-$); MS m/e 454 (M^+, 17%) and 205 (100%); Found: C, 87.38; H, 12.90%. Calcd for $C_{33}H_{58}$: C, 87.14; H, 12.86%.

To a solution of the isopropylidene derivative (**18**; 68 mg) in ether (5 ml), osmium tetraoxide (55 mg) in pyridine (1 ml) was added and the reaction mixture was stirred for 6 h. The solvents were evaporated and ethanol (3 ml), sodium sulfite (406 mg), and water (1 ml) were added to the residue. The reaction mixture was heated under reflux for 2 h and, after cooling, filtered. The precipitate was washed with ethanol. The filtrate and the washings were combined and evaporated under reduced pressure, and the residue purified by column chromatography on silica gel (20 g). Elution with benzene–ether (5: 3) afforded a mixture of the diastereomeric diols (**17**; 27 mg), mp 188—189 °C (crystallized from ether); IR (Nujol) 3400, 1170, 1090, and 960 cm^{-1}; PMR δ ≈0.80 (6H, s and t overlapped, 2×CH_3), 0.90, 0.96, 1.03, 1.16, 1.19, 1.21 (each 3H, s, *t*-CH_3), 1.01 (6H, s, 2×*t*-CH_3), and 4.62 (1H, s, $-\overset{|}{\underset{|}{C}}-OH$; disappeared on addition of D_2O); MS *m/e* 488 (M^+, 31%) and 273 (100%).

To a solution of chromium trioxide (60 mg) in pyridine (52 mg) and methylene dichloride (50 ml), the diols (**17**; 22 mg) in methylene dichloride (5 ml) was added and the reaction mixture was stirred for 15 min. The methylene dichloride solution was separated by decantation and the precipitate was washed with methylene dichloride (100 ml). The supernatant and washings were combined and washed with 5% sodium hydrogencarbonate solution. After usual work-up, the residue was subjected to column chromatographic separation to afford the seco-aldehyde (**8**; 12 mg) and the hydroxy ketone (**5**; 3 mg). The former was identical with the seco-aldehyde (**8**). The latter was completely identical with the photoproduced hydroxy ketone (**5**).

Photochemical Reaction of Friedelin (1) in Ether Containing Acetone-d_6. Friedelin (**1**; 317 mg) was dissolved in ether (150 ml) containing acetone-d_6 (1 ml; 99.8%, Showa-denko Co.) in a quartz vessel, The solution was irradiated for 5 h under the same conditions and then treated as before. The residue was chromatographed on silica gel (50 g), eluted with benzene and fractions containing the keto ether were collected and purified by preparative TLC to give 5α-ethyl-10β-(5,5,5-trideuterio-4-hydroxy-4-trideuteriomethyl-3-oxopentyl)-des-A-friedelane (**5**-d_6; 45 mg); IR (Nujol) 3500, 2220, 1705, and 1130 cm^{-1}; PMR $\delta \approx 0.80$ (6H, s and t overlapped), 0.89, 0.95, 1.03, 1.18 (each 3H, s, *t*-CH_3), 1.00 (6H, s, 2×*t*-CH_3), 2.40—2.75 (2H, m, $-C\underline{H}_2-\overset{|}{C}=O$), and 3.75 (1H, s, -OH); MS *m/e* 492 (M^+, 15%), 477, 463, 446, 443, 428, 413, 325, 313, 301, 273, 218, and 205 (100%).

Photochemical Reaction of 2α,2β,4α-Trideuteriofriedelin (1-d_3*) in Ether Containing Acetone.* 2α,2β,4α-Trideuteriofriedelin (**1**-d_3; 514 mg) was dissolved in ether (450 ml) containing acetone (2 ml) and the solution was irradiated for 5 h. The reaction mixture was treated as usual and separated by column chromatography on silica gel (50 g) and subsequently preparative TLC to afford 5α-(1,1-dideuterioethyl)-10β-(2-deuterio-4-hydroxy-4-methyl-3-oxopentyl)-des-A-friedelane (**5**-d_3; 55 mg); IR (Nujol) 3500, 2160, 2100, 1705, 1130, and 980 cm^{-1}; PMR $\delta \approx 0.80$ (6H, s and t overlapped, 2×CH_3), 0.89, 0.95, 1.02, 1.08 (each 3H, s, *t*-CH_3), 1.00 (6H, s, 2×*t*-CH_3), 1.37 (6H, s, $(C\underline{H}_3)_2C(OH)-$), 2.30 (1H, m, $-CHD-C=O$), and 3.76 (1H, br., -OH); MS *m/e* 489 (M^+, 9%) and 205 (100%).

Degradation of Trideuterio-5α-ethyl-10β-(4-hydroxy-4-methyl-3-oxopentyl)-des-A-friedelane (5-d_3*).* The hydroxy ketone-d_3 (**5**-d_3; 48 mg) in ether (10 ml) was heated under reflux with lithium aluminium hydride (47 mg) and usual treatment and separation gave the diols-d_3 (**17**-d_3; 20 mg); MS *m/e* 419 (M^+, 24%), 476, 458, 324, 301, 273 (100%), 218, and 205.

To the diols-d_3 (**17**-d_3; 18 mg) in benzene (10 ml), was added lead tetraacetate (45 mg) in acetic acid (15 ml) and the reaction mixture was stirred for 3 h. Usual treatment and purification afforded the aldehyde-d_3 (**8**-d_3; 16 mg); PMR $\delta \approx 0.80$ (6H, s and t overlapped, 2×CH_3), 0.90, 0.97, 1.19 (each 3H, s, *t*-CH_3), 1.00 (9H, s, 3×*t*-CH_3), 2.20—2.60 (1H, m, $-C\underline{H}D-CHO$), and 9.73 (1H, d, $J=2$ Hz, $-CHD-C\underline{H}O$); MS *m/e* 431 (M^+, 19%), 416, 301, 273, 218 (100%), and 205.

A mixture of the trideuterio-seco-aldehyde (**8**-d_3; 15 mg) in ether (10 ml) and lithium aluminium hydride (70 mg) was heated under reflux for 3 h. After usual work-up, separation afforded 2,4,4-trideuterio-5α-ethyl-10β-(3-hydroxypropyl)-des-A-friedelane (**9**-d_3; 12 mg); IR (Nujol) 3600, 3450, 2160, 1280, and 1050 cm^{-1}; PMR $\delta \approx 0.79$ (6H, s and t overlapped, 2×CH_3), 0.88, 0.96, 1.19 (each 3H, s, *t*-CH_3), 1.00 (9H, s, 3×*t*-CH_3), 3.95 (2H, d, $J=6$ Hz, $-CHD-C\underline{H}_2OH$); MS *m/e* 433 (M^+, 31%), 428, 402, 301, 279, 273 (100%), 265, 218, and 205. When Eu(dpm)$_3$ was added to a 1.6% (w/v) solution of **9**-d_3 in $CDCl_3$ [Eu(dpm)$_3$/**9**-d_3=1.1 (in molar ratio)], $C_{4)}-CH_3$ signal appeared at δ 2.12 as a singlet. Under the same conditions, $C_{(4)}-CH_3$ of non-labeled alcohol (**9**) resonated at δ 2.12 as a triplet ($J=7$ Hz).

Photochemical Reaction of Friedelin (1) in Acetone. Friedelin (**1**; 705 mg) in acetone (88 ml) in a Pyrex vessel was photolyzed. The rate of the photolysis was very slow and the photolysate after 27 h-irradiation was found to consist of recovered friedelin (**1**; 545 mg), the hydroxy ketone (**5**; 12 mg), and an unknown hydroxy dicarbonyl compound (32 mg).

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