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Studies on the Neutral Constituents of *Pachysandra terminalis* Sieb. *et* Zucc. VII.[1] Structures of Acid-induced Rearrangement Products of 16-Keto-friedel-3-ene[2]

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The structures of the rearrangement products B (III) and C (IV) of 16-keto-friedel-3-ene (I) (a derivative of pachysandiol-B), obtained upon treatment with zinc chloride, were determined cn the basis of chemical and spectroscopic evidence, especially by means of the homonuclear INDOR technique.

Keywords——*Pachysandra terminalis*; triterpene; acid-induced rearrangement; 16-keto-friedel-3-ene; friedelin; homonuclear INDOR; NOE

In a previous paper,[4] we reported that the reaction of 16-keto-friedel-3-ene (I) with zinc chloride in acetic acid gave 16-keto-18α-olean-12-ene (II) (product A) and two unidentified compounds (products B and C). This paper gives full details of the structure elucidation of these rearranged products by chemical and spectroscopic analyses, especially by the application of the homonuclear internuclear double resonance (INDOR) technique.[5]

As described in the experimental section, the rearranged products B (III) and C (IV) were obtained as a mixture which could not be separated at this step, but after reduction with lithium aluminum hydride the resulting alcohols were separated by preparative thin-layer chromatography (TLC) to afford a mixture of two isomeric alcohols (Va and VIa) and another alcohol (VIIa). Oxidation of these alcohols with chromium trioxide in pyridine regenerated product B (III), mp 208—212°, and product C (IV), mp 233—235°, respectively.

Products B (III) and C (IV) were analyzed as $C_{30}H_{48}O$ and both showed a carbonyl band (1680 cm^{-1} for III and 1695 cm^{-1} for IV) in the infrared (IR) spectra and no olefinic proton signal in the nuclear magnetic resonance (NMR) spectra, suggesting the existence of a tetra-substituted double bond in the molecules.

Product C (IV) was also obtained when 16-keto-18α-olean-12-ene (II) was treated with zinc chloride in acetic acid. These two compounds (II and IV) were possibly in an equilibrium under these reaction conditions.[6]

On the other hand, treatment of product B (III) again with zinc chloride gave 16-keto-18α-olean-12-ene (II). Thus, product B must be an intermediate in the rearrangement, and two possible structures (III and X) can be deduced.

1) Part VI: T. Kikuchi and M. Niwa, *Yakugaku Zasshi*, **93**, 1378 (1973).
2) A preliminary account of a part of this work has appeared in *Tetrahedron Lett.*, **1973**, 1987.
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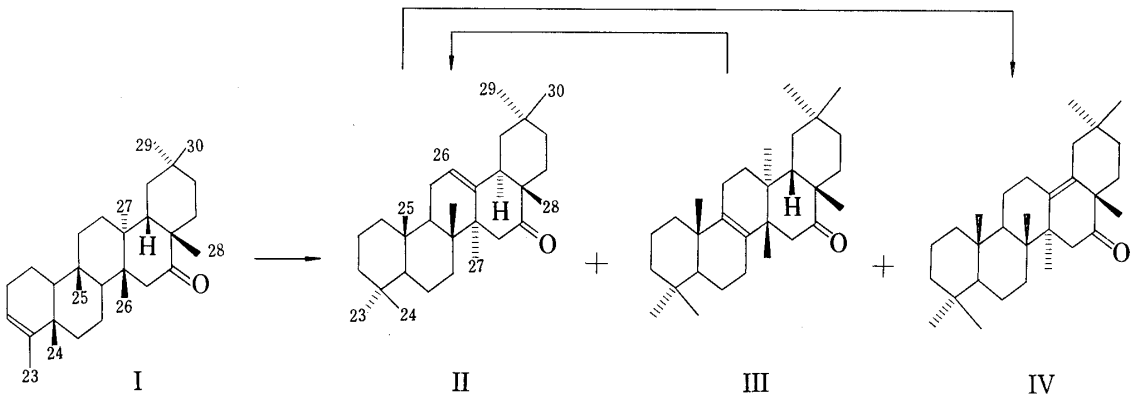
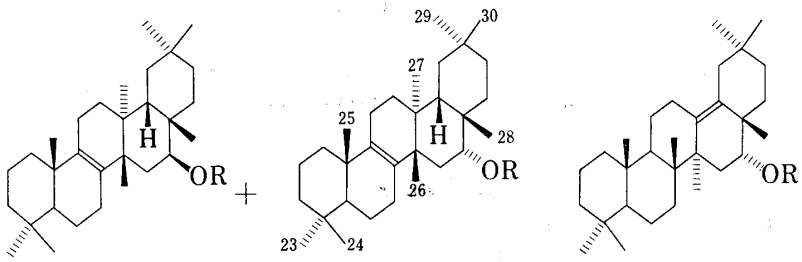
4) T. Kikuchi, M. Takayama, T. Toyoda, M. Arimoto, and M. Niwa, *Chem. Pharm. Bull.*, **21**, 2243 (1973).
5) E.B. Baker, *J. Chem. Phys.*, **37**, 911 (1962); O. Sciacovelli, W. von Philipsborn, C. Amith, and D. Ginsburg, *Tetrahedron*, **26**, 4589 (1970); T. Kikuchi, T. Yokoi, M. Niwa, and T. Shingu, *Chem. Pharm. Bull.*, **25**, 2078 (1977) and references cited therein.
6) *a*) J.L. Courtney, R.M. Gascoigne, and A.Z. Szumer, *J. Chem. Soc.*, **1958**, 881; *b*) G. Brownlie, M.B.E. Fayez, F.S. Spring, R. Stevenson, and W.S. Strachan, *ibid.*, **1956**, 1377.



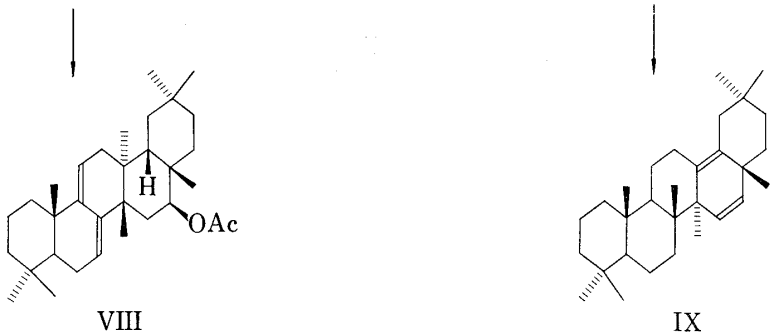
I II III IV



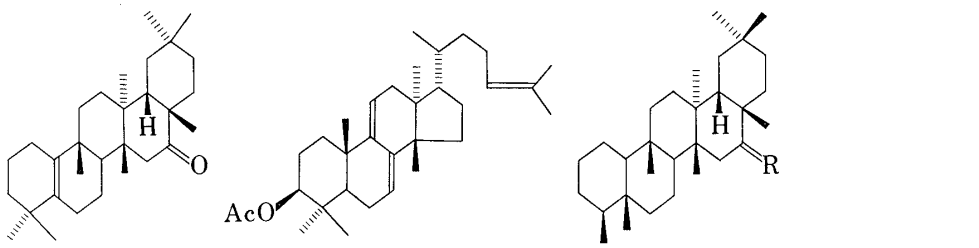
Va : R=H
Vb : R=Ac

VIa : R=H
VIb : R=Ac

VIIa : R=H
VIIb : R=Ac



VIII IX



X XI

XIIa : R=  (D-ring : boat)

XIIb : R= 

Chart 1

Lithium aluminum hydride reduction of product B gave a mixture of epimeric alcohols (Va and VIa), the same as that mentioned above, which showed a single spot on TLC. After acetylation, the mixture was separated by preparative TLC to afford an acetate (Vb), mp 182—185°, and its epimer (VIb), mp 189—192°, in an approximate ratio of 1: 2. Treatment of Vb and VIb with lithium aluminum hydride gave rise to the corresponding alcohols, Va and VIa, respectively. Both Va and VIa regenerated product B (III) upon chromium trioxide oxidation.

In the NMR spectrum, the minor acetate (Vb) exhibited a triplet signal (J=9 Hz) at δ 5.27 for the C (16)-hydrogen geminal to the acetoxyl group, while the major acetate (VIb) gave

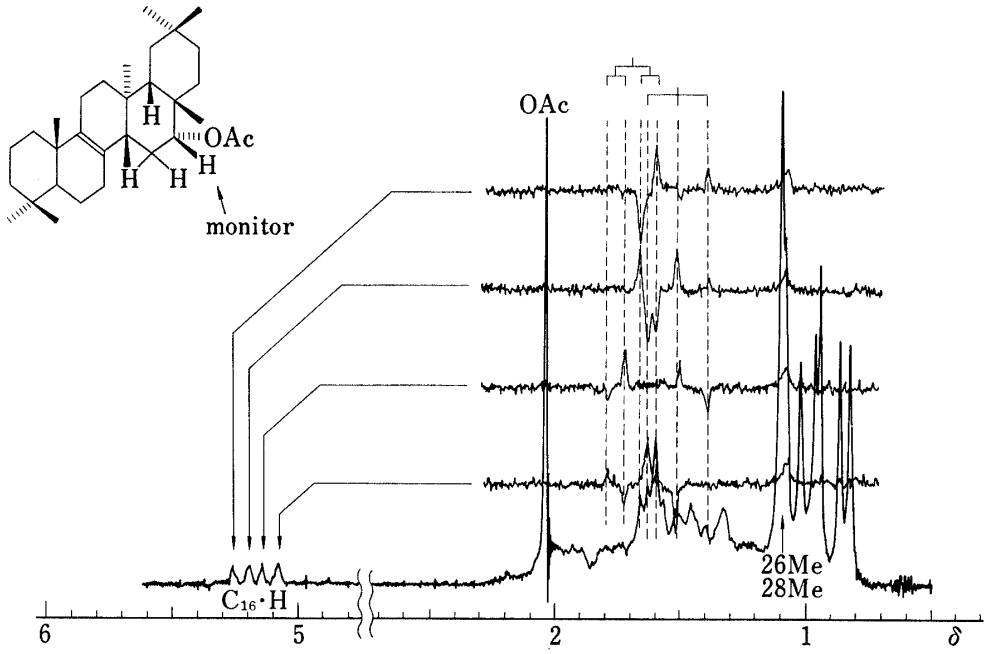


Fig. 1. Normal and INDOR Spectra of the Acetate (VIb) using the Four Transitions of C(16)-H as Monitor Lines

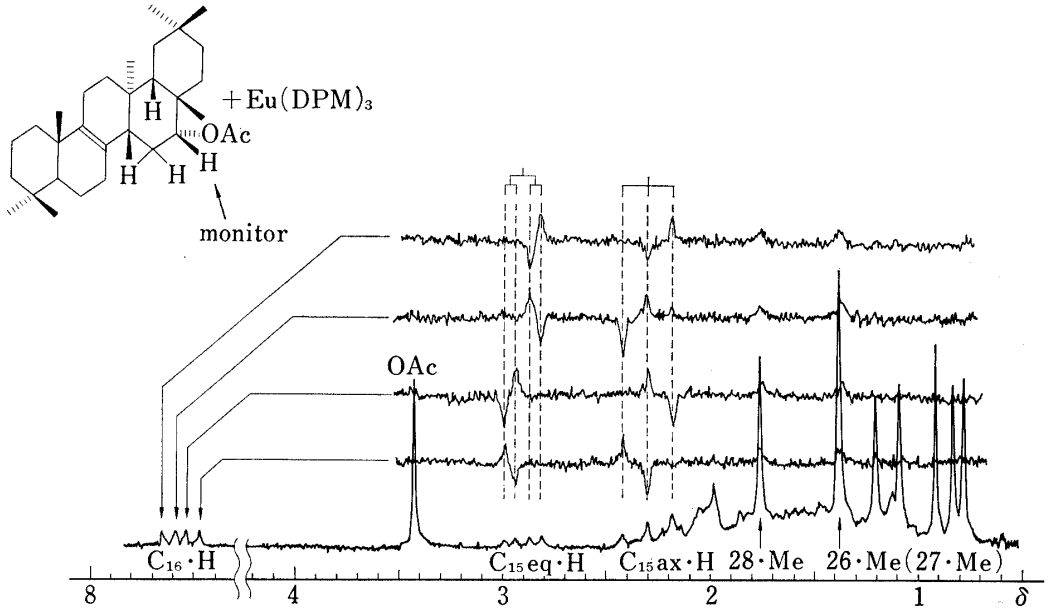


Fig. 2. Normal and INDOR Spectra of the Acetate (VIb) using the Four Transitions of C(16)-H as Monitor Lines in the Presence of $Eu(DPM)_3$ (0.15 mol equiv.)

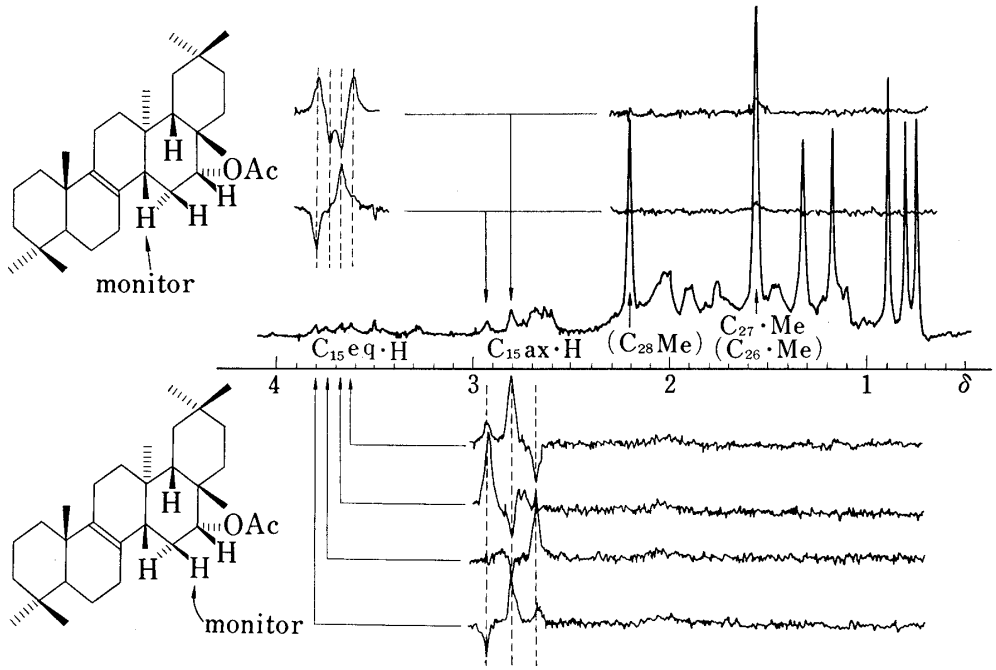


Fig. 3. INDOR Spectra of the Acetate (VIb) using Transitions of C(15)ax-H and Transitions of C(15)eq-H as Monitor Lines in the Presence of $Eu(DPM)_3$ (0.25 mol equiv.)

a double doublet (J=6.5, 10.5 Hz) at δ 5.18, indicating that the acetoxyl groups in these compounds are both equatorial. The configuration of the acetoxyl group in Vb was assigned to be β and that in VIb to be α by comparison of the chemical shifts and splitting patterns of the C (16)-hydrogens with those of 16β- and 16α-acetoxyfriedelanes (XIIa and XIIb).[4,7]

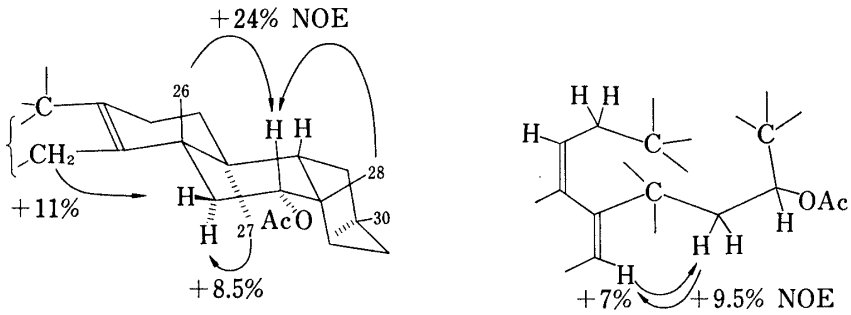
Reaction of the above acetate (Vb) with selenium dioxide gave an oily diene (VIII), $C_{32}H_{50}O_2$, in 62% yield, whereas the same reaction of the acetate (VIb) resulted in recovery of the starting material. The NMR spectrum of VIII exhibited broad signals for two olefinic protons, newly introduced, at δ 5.59 and δ 5.25 and its ultraviolet (UV) spectrum showed absorption bands for a heteroannular conj. diene at 235 (sh), 241 (ε 11,030), and 248 (sh) nm, which are in excellent agreement with the reported values for eupha-7,9(11),24-trien-3β-ol acetate (XI)[8] produced by the selenium dioxide oxidation of eupha-7,24-dien-3β-ol acetate.

Next, in order to obtain more detailed information, we performed INDOR studies of the acetate VIb, which has the D-ring in a chair conformation. As illustrated in Fig. 1, monitoring the four lines of C(16)–H gave INDOR signals arising from C(15)–H_2 in the δ 1.4—1.8 region and a small peak at δ 1.08. The latter peak could be ascribed to the nuclear Overhauser effect(NOE) between the C(16)–H and the 26-methyl and 28-methyl groups, since irradiation at δ 1.08 gave a 24% NOE increase in the C(16)–H signal (Chart 2).

In the presence of a lanthanide shift reagent, tris(dipivaloylmethanato)europium(III) ($Eu(DPM)_3$) (0.15 mol equiv.), the INDOR signals and the NOE peaks were clearly resolved, as shown in Fig. 2. The peaks at δ 1.37 and 1.75 are ascribable to the NOE's due to the 26- and 28-methyls, respectively, on the basis of their shift behavior. When the two lines of the C(15)ax-H were monitored in the presence of 0.25 mol equiv. of the shift reagent (Fig. 3), INDOR signals of the C(15)eq–H were observed at δ 3.70, and at the same time an NOE peak appeared at the signal of δ 1.56, which could be identified as the 27-methyl signal, just overlapping the 26-methyl signal. On addition of more shift reagent, the above methyl signal was

7) N. Masaki, M. Niwa, and T. Kikuchi, *J. Chem. Soc.* (Perkin II), **1975**, 610.
8) D.H.R. Barton, J.F. McGhie, M.K. Pradhan, and S.A. Knight, *J. Chem. Soc.*, **1955**, 876.

separated into two singlets. In this state, INDOR spectra were measured using the lines of C(15)ax–H as monitor lines; an NOE peak was seen at the lower-side singlet, which is therefore assigned to the 27-methyl group. In turn, irradiation at this 27-methyl signal gave an 8.5% increase in the signal intensity of C(15)ax–H (Chart 2). Next, monitoring of the quartet of C(15)eq–H gave INDOR signals for C(15)ax–H around δ 2.68—2.93 and a broad peak at δ 2.06 (see Fig. 3), which might be ascribed to the NOE due to the C(7)-protons. Irradiation at δ 2.06 gave an 11% NOE increase in the C(15)eq–H signal. However, further experiments monitoring the C(7)-proton signal gave very complex INDOR signals which could not be analyzed.



VIb XIII

Chart 2

Next, we carried out INDOR experiments with the diene acetate (VIII), in which the D-ring is thought to have a boat conformation by analogy with Vb. The NMR spectrum of VIII showed broad signals for two olefinic protons at δ 5.59 and δ 5.25; the latter signal partly overlapped a triplet (J=9 Hz) at δ 5.20 for the C(16)-hydrogen geminal to the acetoxyl group. As seen in Fig. 4, monitoring the triplet lines of C(16)–H led us to find the signals

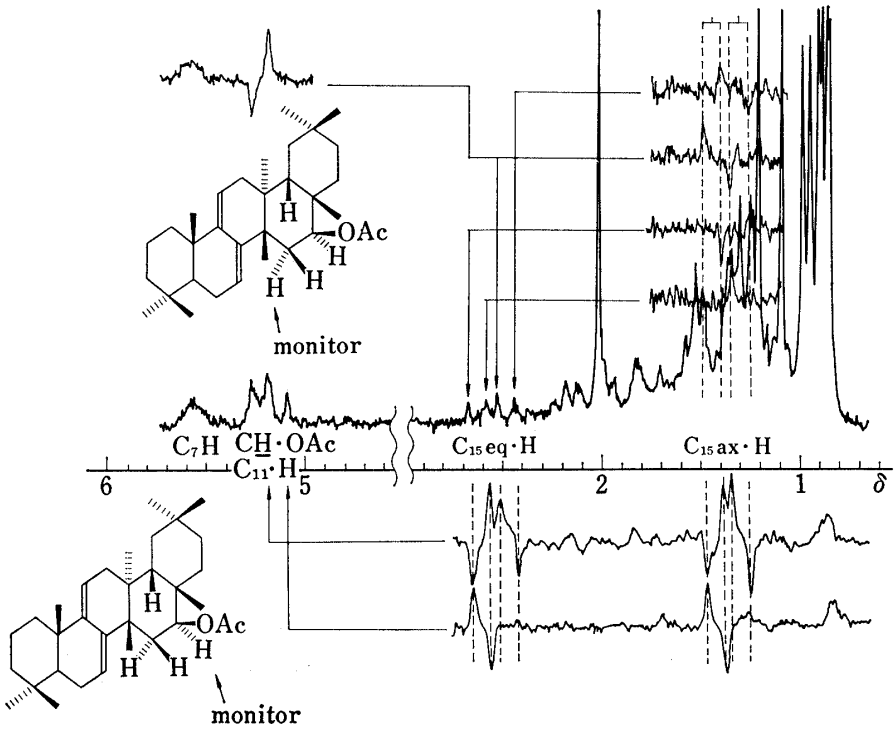


Fig. 4. Normal and INDOR Spectra of the Diene Acetate (VIII) using Two Transitions of C(16)-H and Four Transitions of C(15) eq-H as Monitor Lines

of C(15)eq- and ax-hydrogens. A small NOE peak was also observed at the methyl signal position of δ 0.87, which may be ascribed to the 27-methyl. When the lines of C(15)eq–H were monitored, an NOE peak appeared at the position of the olefinic signal at lower field (δ 5.59), in addition to INDOR signals arising from the C(15)ax- and C(16)-protons. Moreover, irradiation at the C(15)eq–H signal gave a 9.5% increase in the signal intensity of the olefinic proton at δ 5.59, while conversely, irradiation at the latter signal gave a 7% NOE increase in the former. Accordingly, this olefinic hydrogen should be assigned to the C(7)-hydrogen, and therefore the $\Delta^{7,9(11)}$-diene structure was suggested for this compound (Chart 2).

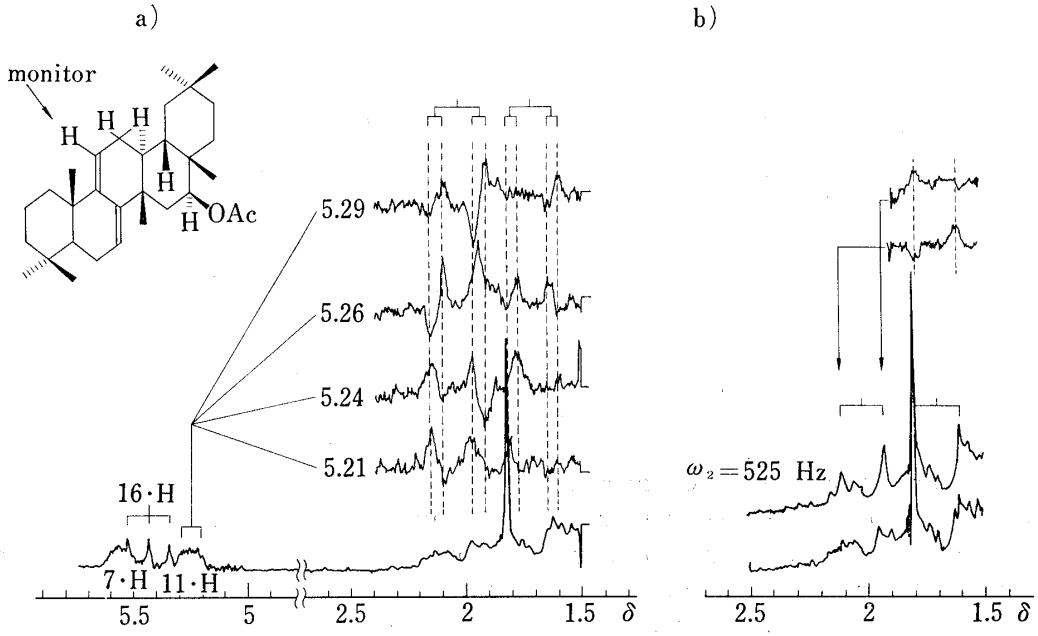


Fig. 5. NMR Spectra of the Diene Acetate (VIII) in C_6D_6

a) Normal and INDOR spectra using the four transitions of C(11)-H as monitor lines.
b) Normal, decoupled (ω_2=525 Hz), and INDOR spectra.

Further INDOR experiments using the signal of another olefinic proton (δ 5.25) gave complex spectra which could not be analyzed, probably because of overlapping of the olefinic signal with the C(16)-hydrogen signal in $CDCl_3$ solution. Instead, they were resolved in C_6D_6 solution, and the olefinic proton signal appeared at δ 5.25 as a broad peak. The INDOR experiment monitoring this signal disclosed two sets of quartets due to methylene hydrogens (Fig. 5a).

Decoupling of the olefinic proton by irradiation at δ 5.25 simplified the spectrum, in which the methylene signal occurred as an AB quartet (δ 1.67 and δ 2.01, J=18 Hz), partly obscured by overlapping with other signals, as shown in Fig. 5b. Under these conditions, monitoring two lines of this AB quartet confirmed the positions of the other two lines (Fig. 5b). Thus, the presence of the partial structure XIII in the diene acetate (VIII) was established.

Based on the above observations, the structure of the diene acetate can be assigned as VIII, and hence the rearranged product B as III. It should be emphasized that product B (III) is the first reported example of an intermediate having a double bond at C(8)–C(9) in friedelene-oleanene rearrangement.[9]

We next examined the structure of the rearranged product C (IV). Lithium aluminum hydride reduction of IV gave solely the alcohol (VIIa) mentioned above, mp 196—198°, whose

9) Such compounds as III have hitherto been considered to be too unstable to be isolated, since the B- and C-rings would be in half-boat conformations. See reference 6*a*.

NMR spectrum showed a double doublet (J=5.0, 3.5 Hz) at δ 3.58 due to a proton on the hydroxyl-bearing carbon, indicating that the hydroxyl group is in axial orientation.

Furthermore, it is noteworthy that one of the *tertiary* methyl signals in VIIa appeared at fairly low field (δ 1.38), while the corresponding signal in the NMR spectrum of the acetate (VIIb) showed an upfield shift to δ 1.22. This suggests that the methyl group concerned and the hydroxyl are in a 1,3-diaxial relationship[10] and therefore occupy the 14α- and 16α-positions, respectively, since in the case of the alternative 14β,16β-arrangement, the D-ring must have a boat form with C(16)–OH equatorial orientation.[4]

Treatment of VIIa with phosphorus oxychloride gave a dehydrated compound (IX), mp 190—193°, which showed a singlet signal due to two olefinic protons at δ 5.34. Attempts to carry out catalytic hydrogenation of IX in the hope of derivatizing it to a known compound resulted in recovery of the starting material. However, on the basis of the above findings and consideration of the reported equilibrium between 18α-olean-12-ene and olean-13(18)-ene under acidic conditions,[6] the structure of product C can be assigned as IV.

Experimental

All melting points were measured with a Kofler-type apparatus and are uncorrected. All specific rotations were measured in $CHCl_3$ solutions. IR spectra were measured for solutions in $CHCl_3$, unless otherwise stated. NMR spectra were taken on a Varian Associates A-60 spectrometer in $CDCl_3$ solutions using tetramethylsilane as an internal reference, and chemical shifts are recorded in δ values. Unless otherwise specified, INDOR spectra were measured in $CDCl_3$ solution using a Varian HA-100D spectrometer which was modified for INDOR experiments according to Jenkins and Phillips (P.N. Jenkins and L. Phillips, *J. Phys.* (E), **4**, 530 (1972)). Mass spectral determinations were performed on a Hitachi RMU-6D or a Hitachi RMU-7MG mass spectrometer with a direct inlet system. TLC was carried out using Merck Kieselgel G. acc. to Stahl. Coloring reagent: $Ce(SO_4)_2$ in 10% H_2SO_4. Preparative thin-layer chromatography was performed on Merck Kieselgel GF_{254} with $CHCl_3$, benzene–$CHCl_3$ or benzene, and plates were examined under UV light (for UV-absorbing materials on GF_{254} plates). For the extraction of substances from the Kieselgel, methylene chloride was used.

Isolation of the Rearrangement Products B (III) and C (IV)——i) Reaction of 16-Keto-friedel-3-ene (I) with Zinc Chloride: Zinc chloride (freshly fused and crushed) (9.4 g) was added to a solution of I (330 mg) in AcOH (15 ml); the mixture was heated at 90° under vigorous stirring for 20 min. The mixture was diluted with water, then extracted with ether, and the ethereal extract was washed with dil. Na_2CO_3, dried (K_2CO_3), and concentrated. The residue (315 mg) was separated by preparative TLC into two fractions. The less polar fraction (98 mg) was recrystallized from CH_2Cl_2–MeOH to give 16-keto-18α-olean-12-ene (II) (90 mg), mp 192—193°. The more polar fraction (183 mg) was a mixture of products B (III) and C(IV), which showed a single spot on TLC.

ii) Lithium Aluminum Hydride Reduction of the Mixture (III and IV): The above mixture (III and IV) (158 mg) was treated with excess $LiAlH_4$ in boiling THF (5 ml) for 7 hr. After decomposition of the excess reagent, the product was taken up in CH_2Cl_2. The solution was dried ($MgSO_4$) and concentrated. The residue (155 mg) was separated by preparative TLC into two fractions. The more polar fraction was a mixture of two epimeric alcohols (Va and VIa) (140 mg). The less polar fraction was recrystallized from ether–MeOH to give another alcohol (VIIa) (10 mg), mp 195—196°.

iii) Product B (III): A solution of the mixture of two epimeric alcohols (Va and VIa) (22 mg) in pyridine (1.5 ml) was added to a suspension of CrO_3 (10 mg) in pyridine (1 ml), and the mixture was stirred for 2 hr at room temperature. The reaction mixture was diluted with water and extracted with CH_2Cl_2. The extract was washed with dil. HCl and dil. Na_2CO_3, dried ($MgSO_4$), and concentrated. The residue (22 mg) was purified by preparative TLC and then recrystallized from CH_2Cl_2–MeOH to afford colorless prisms (III) (17 mg), mp 208—212°. $[\alpha]_D^{25}$ +41.9° (c=1.0). IR ν_{max} cm^{-1}: 1680. NMR δ: 2.43 (2H, broad s, CO–C<u>H</u>$_2$), 0.80—1.27 (8×*tert*-CH_3). ORD: −Cotton effect ($[\phi]_{313}$ −3480, $[\phi]_{260}$ +5660). MS m/e: 424 (M^+). *Anal.* Calcd for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 85.07; H, 11.65.

iv) Product C (IV): The alcohol (VIIa) (30 mg) was added to a suspension of CrO_3 (15 mg) in pyridine (2 ml), and the mixture was stirred for 40 min at room temperature. The reaction mixture was worked up as described above to give a crude product (29 mg). Recrystallization from ether–MeOH afforded colorless

10) Y. Kawazoe, Y. Sato, M. Natsume, H. Hasegawa, T. Okamoto, and K. Tsuda, *Chem. Pharm. Bull.*, **10**, 338 (1962); Y. Kawazoe, Y. Sato, T. Okamoto, and K. Tsuda, *ibid.*, **11**, 328 (1963); T. Okamoto and Y. Kawazoe, *ibid.*, **11**, 648 (1963).

prisms (IV) (25 mg), mp 233—235°. $[\alpha]_D^{24}$ −72.7° (c=1.0). IR ν_{max} cm^{-1}: 1695. NMR δ: 2.90, 1.96 (each 1H, ABq, J=12.5 Hz, CO-C<u>H</u>$_2$-), 0.69—1.25 (8×*tert*-CH$_3$). MS m/e: 424 (M$^+$). *Anal.* Calcd for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 84.59; H, 11.53.

Reaction of 16-Keto-18α-olean-12-ene (II) with Zinc Chloride in Acetic Acid——Crushed fused $ZnCl_2$ (3 g) was added to a solution of II (105 mg) in AcOH (5 ml), and the mixture was heated at 90° under vigorous stirring for 5 hr. The reaction mixture was treated in the usual manner and the crude product (105 mg) was separated by preparative TLC to give a rearranged product (IV) (37 mg) and the starting material (II) (40 mg). Recrystallization of the former product (IV) from CH_2Cl_2–MeOH afforded colorless prisms (33 mg), mp 233—235°. This compound was identical with product C (IV) described above on comparison by TLC, IR (KBr), and NMR.

Reaction of the Rearranged Product B (III) with Zinc Chloride——Product B (III) (13 mg) was treated with $ZnCl_2$ (400 mg) in AcOH (3 ml) at 90° for 7 hr as described above. Usual work-up gave a crude product (13 mg), which was purified by preparative TLC and then recrystallized from CH_2Cl_2–MeOH to afford colorless plates (II) (4 mg), mp 190—192°. This product was identified as 16-keto-18α-olean-12-ene (II) by TLC and IR (KBr) comparisons with the authentic material.

Lithium Aluminum Hydride Reduction of Product B (III) and Subsequent Acetylation——Product B (III) (170 mg) was reduced with excess $LiAlH_4$ in the usual manner to give a mixture of the epimeric alcohols (Va and VIa) (160 mg). This was treated with Ac_2O-pyridine (each 1 ml) overnight at room temperature. The excess reagent was decomposed by addition of water and the product was taken up in CH_2Cl_2. The CH_2Cl_2 solution was washed successively with dil. HCl and dil. Na_2CO_3, dried ($MgSO_4$), and concentrated. The residue (150 mg) was separated by preparative TLC into two fractions. The less polar fraction (44 mg) was recrystallized from ether–MeOH to give colorless needles (Vb), mp 182—185°. High resolution mass spectrum m/e, Calcd for $C_{32}H_{52}O_2$ (M$^+$): 468.3964. Found: 468.3903. IR ν_{max} cm^{-1}: 1715, 1260. NMR δ: 5.27 (1H, t, J=9 Hz, C<u>H</u>-OAc), 1.99 (3H, s, Ac), 0.83—1.28 (8×*tert*-CH$_3$). The more polar fraction (79 mg) was recrystallized from ether–MeOH to give colorless needles (VIb), mp 189—192°. High resolution mass spectrum m/e, Calcd for $C_{32}H_{52}O_2$ (M$^+$): 468.3964. Found: 468.3971. IR ν_{max} cm^{-1}: 1720, 1255 NMR δ: 5.18 (1H, dd, J=6.5, 10.5 Hz, C<u>H</u>-OAc), 2.04 (3H, s, Ac), 0.83—1.10 (8×*tert*-CH$_3$).

Lithium Aluminum Hydride Reduction of the Acetate (Vb) and Subsequent Chromium Trioxide Oxidation——The acetate (Vb) (44 mg) was treated with excess $LiAlH_4$ in boiling ether (9 ml) for 4 hr. Usual work-up gave the corresponding alcohol (Va) (38 mg), which was recrystallized from ether–MeOH to afford colorless needles, mp 204—207°. High resolution mass spectrum m/e, Calcd for $C_{30}H_{50}O$ (M$^+$): 426.3859. Found: 426.3901. IR ν_{max} cm^{-1}: 3600, 3450. NMR δ: 4.07 (1H, t, J=9 Hz, C<u>H</u>-OH), 0.84—1.25 (8×*tert*-CH$_3$).

A solution of the above alcohol (Va) (30 mg) in pyridine (1.5 ml) was added to a suspension of CrO_3 (10 mg) in pyridine (1 ml), and the mixture was stirred for 40 min at room temperature. The product (30 mg), isolated in the usual manner, was recrystallized from ether–MeOH to give colorless prisms (III) (26 mg), mp 218—221°. This was identical with the rearrangement product B (III) on comparison by TLC and IR (KBr).

Lithium Aluminum Hydride Reduction of the Acetate (VIb) and Subsequent Chromium Trioxide Oxidation——The acetate (VIb) (79 mg) was treated with excess $LiAlH_4$ in boiling ether (10 ml) for 4 hr and then worked up as usual to give an alcohol (VIa) (71 mg), which was recrystallized from ether to afford colorless needles, mp 121—125°. High resolution mass spectrum m/e, Calcd for $C_{30}H_{50}O$ (M$^+$): 426.3859. Found: 426.3866. IR ν_{max} cm^{-1}: 3600, 3450. NMR δ: 3.88 (1H, dd, J=6, 11 Hz, C<u>H</u>-OH), 0.84—1.17 (8×*tert*-CH$_3$). This alcohol (61 mg) in pyridine (2 ml) was treated with CrO_3 (20 mg) at room temperature for 30 min. The product (56 mg), isolated in the usual way, was recrystallized from ether–MeOH to give colorless prisms (III) (49 mg), mp 215—218°. Its identity was confirmed by TLC and IR (KBr) comparisons with product B (III).

Selenium Dioxide Oxidation of the Acetate (Vb)——A solution of SeO_2 (20 mg) in AcOH (2 ml) and H_2O (2 drops) was added to a solution of the acetate (Vb) (13 mg) in AcOH (3 ml), and the mixture was refluxed under stirring for 10 hr. The dark brown precipitate was filtered off and the filtrate was concentrated under reduced pressure. The residue was chromatographed on alumina (0.7×5 cm), and elution with benzene gave an oily substance which was purified further by preparative TLC to afford a colorless oily diene acetate (VIII) (8 mg). MS m/e: 466 (M$^+$) ($C_{32}H_{50}O_2$). IR ν_{max} cm^{-1}: 1720, 1660, 1250. UV λ_{max}^{EtOH} nm: 235 (sh), 241 (ε 11030), 248 (sh). NMR δ: 5.59 (1H, broad, CH=C), 5.25 (1H, broad, CH=C), 5.20 (1H, t, J=9 Hz, C<u>H</u>-OAc), 2.02 (3H, s, Ac), 0.87—1.23 (8×*tert*-CH$_3$).

Lithium Aluminum Hydride Reduction of Product C (IV) and Subsequent Acetylation—The rearranged product C (IV) (14 mg) was treated with $LiAlH_4$ in boiling THF (5 ml) for 2 hr and then worked up as usual. Purification of the crude product (14 mg) by preparative TLC gave an alcohol (VIIa) (11 mg), which was recrystallized from ether–MeOH to afford colorless prisms, mp 196—198°. IR ν_{max}^{KBr} cm^{-1}: 3500, 3350, NMR δ: 3.58 (1H, dd, J=3.5, 5.0 Hz, C<u>H</u>-OH), 0.76—1.37 (8×*tert*-CH$_3$). High resolution mass spectrum m/e, Calcd for $C_{30}H_{50}O$ (M$^+$): 426.3859. Found: 426.3865. This compound was identical with the alcohol (VIIa), described above, on the basis of TLC and IR (KBr) comparisons.

The above alcohol (VIIa) (11 mg) was acetylated with acetic anhydride–pyridine (each 0.5 ml) in the usual manner to give an oily acetate (VIIb) (12 mg). MS m/e: 468 (M$^+$) ($C_{32}H_{52}O_2$). IR ν_{max} cm^{-1}: 1715,

1250. NMR δ: 4.82 (1H, dd, J=3.5, 5.0 Hz, C<u>H</u>–OAc), 2.02 (3H, s, Ac), 0.77—1.27 (8×*tert*-CH_3).

Reaction of the Alcohol (VIIa) with Phosphorus Oxychloride——Phosphorus oxychloride (4 drops) was added to a chilled solution of VIIa (31 mg) in pyridine (1 ml), and the mixture was kept overnight at room temperature. After decomposing the excess reagent by careful addition of ice-water, the mixture was extracted with ether. The extract was washed successively with dil. HCl and dil. Na_2CO_3, dried ($MgSO_4$), and concentrated. Recrystallization of the residue (30 mg) from ether–MeOH gave a dehydrated product (IX) as colorless needles (25 mg), mp 190—193°. High resolution mass spectrum *m/e*, Calcd for $C_{30}H_{48}$ (M^+): 408.3753. Found: 408.3821. IR ν_{max}^{KBr} cm^{-1}: 760. NMR δ: 5.34 (2H, s, C<u>H</u>=C<u>H</u>), 0.72—1.19 (8×*tert*-CH_3).

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