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Studies on the Neutral Constituents of *Pachysandra terminalis* Sieb. *et* Zucc. IX.[1] Structures of Pachysandienol-A and -B, Novel-Type Triterpenes related to Friedelin

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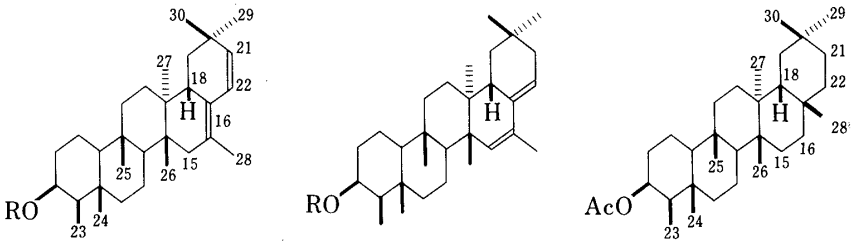
Two novel-type triterpenes, pachysandienol-A and -B, were isolated from *Pachysandra terminalis* Sieb. *et* Zucc., and were proved to have the structures Ia and IIa, respectively, by means of chemical and spectroscopic studies. Ia and IIa are the first examples among natural products of 28-nor-16-methyl-friedelane derivatives.

Keywords——pachysandienol-A; pachysandienol-B; triterpene; *Pachysandra terminalis* Sieb. *et* Zucc.; 28-nor-16-methyl-friedelane; INDOR; methyl signal assignment

In previous papers,[2] we reported the isolation and characterization of new triterpenes, tentatively named compound-IV and compound-IIIb, from the neutral fraction of *Pachysandra terminalis* Sieb. *et* Zucc. (Japanese name: fukki-so), along with other several triterpenes and sterols. We proposed the names pachysandienol-A and -B for compound-IV and compound-IIIb, respectively, and studied the structures of these triterpenes. As a result, pachysandienol-A and -B were proved to be Ia and IIa, respectively, which have a previously unreported, 28-methyl-migrated friedelane skeleton. This paper describes the structure elucidation in detail.



Ia : R=H
Ib : R=Ac

IIa : R=H
IIb : R=Ac

III

Chart 1

Pachysandienol-A (Ia) was purified as its acetate (Ib), mp 260—261°C, and the pure dienol (Ia), mp 211—213°C, $[\alpha]_D$ +153.1°, ν_{max} 3600 cm^{-1}, was obtained by alkaline hydrolysis of the acetate. Microanalytical and mass spectral (MS) data of Ia are consistent with the molecular formula $C_{30}H_{48}O$. The nuclear magnetic resonance (NMR) spectrum of the acetate (Ib) shows the presence of two double bonds (δ 6.25 and 5.39, each 1H, doublet, J=10 Hz, olefinic protons; and δ 1.68, 3H, d, J=1 Hz, vinyl CH_3), an acetoxyl group (δ 2.03, 3H, s, Ac, and δ 4.90, 1H, m, C<u>H</u>–OAc), six *tert*-methyl groups (δ 1.02—0.79), and a *sec*-methyl group

(δ 0.82, d, J=6 Hz). As will be mentioned later, this *sec*-methyl signal shows the largest lanthanide-induced shift among eight methyl groups, suggesting that the *sec*-methyl is vicinal to the acetoxyl group, as in epifriedelanol acetate (III).[3] The ultraviolet (UV) spectrum of Ib exhibits absorption maxima at 240 (sh), 245 (ε: 24400), and 252 (sh) nm, characteristic of a heteroannular conjugated diene structure.

Pachysandienol-B (IIa) was also isolated as its acetate (IIb), mp 228—229°C, $[\alpha]_D$ +76.4°, and $LiAlH_4$ reduction of the latter (IIb) gave a pure sample (IIa), $C_{30}H_{48}O$, mp 238—241°C, $[\alpha]_D$ +89.5°, ν_{max} 3600 cm^{-1}. The NMR spectrum of IIb shows a singlet at δ 2.03 due to an acetoxyl group, a broad signal at δ 4.90 due to a hydrogen geminal to the acetoxyl group, two multiplets at δ 5.70 and 5.62 due to olefinic protons, a doublet at δ 1.73 (J=1.5 Hz) due to a vinyl methyl, and partially overlapped signals at δ 1.00—0.74 due to seven methyl groups, one of which must be a *sec*-methyl group since a pseudo-contact shift study revealed the presence of a doublet methyl signal as will be mentioned later. The UV spectrum of IIb also exhibitsabsorption maxima at 239 (sh), 246 (ε: 17700), and 253 (sh) nm, characteristic of a heteroannular diene.

These observations suggest that Ia and IIa might be pentacyclic triterpenes with a conjugated diene, and might be regio-isomeric to each other.

Thus, we carried out internuclear double resonance (INDOR) experiments[4] in order to obtain more detailed information about the diene system.

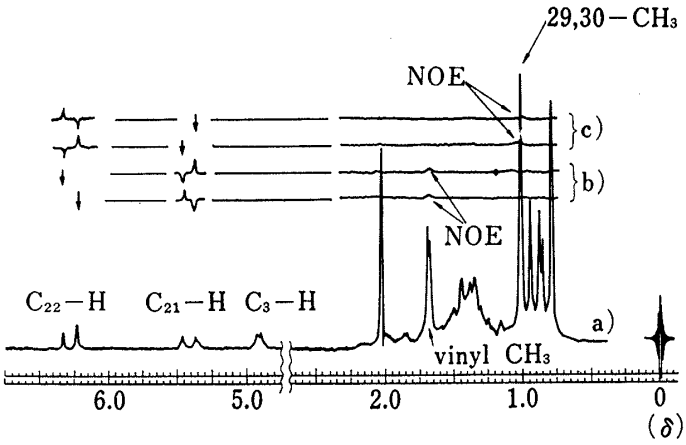


Fig. 1. INDOR Experiments with Pachysandienol-A Acetate (Ib)

a) 100 MHz NMR spectrum of Ib, b) INDOR spectra using the C_{22}–H signals as monitor lines, c) INDOR spectra using the C_{21}–H signals as monitor lines.

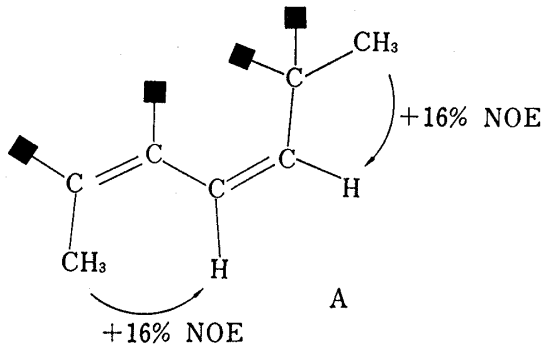


Chart 2

First, INDOR experiments were done with Ib. When each line of the lower-field olefinic proton doublet (δ 6.30 and 6.20) was monitored, a small peak was observed at δ 1.7, along with the INDOR signals at δ 5.44 and 5.34 due to spin-spin coupling (Fig. 1b). In turn, monitoring each line of the higher-field olefinic proton doublet (δ 5.44 and 5.34) gave a small peak at δ 1.02 together with the ordinary INDOR signals (δ 6.30 and 6.20) (Fig. 1c). These small peaks are thought to be due to the nuclear Overhauser effect (NOE) between the olefinic and vinyl methyl protons and between the olefinic and *tert*-methyl protons. Eventually, these NOE's were confirmed by conventional measurements: irradiation at δ 1.68 gave a 16% increase of signal intensity of the olefinic proton at δ 6.25 and irradiation of the *tert*-methyl protons at δ 1.02 gave a 16% NOE increase of the olefinic proton at δ 5.39.

The above observations suggest that Ib has the partial structure A (Chart 2).

At this stage, the following chemical reactions were applied to Ib. Treatment of Ib with *m*-chloroperbenzoic acid afforded an *m*-chlorobenzoyloxy-alcohol (IV),[5] $C_{39}H_{55}ClO_5$,

mp 145—147°C, which exhibits hydroxyl absorptions at 3600 and 3500 cm^{-1} in the infrared (IR) spectrum. The NMR spectrum of IV shows no olefinic proton, but signals of four aromatic protons (δ 8.00—7.30), a proton geminal to the benzoyloxy group (δ 6.07, d, J=3 Hz), and a proton geminal to the hydroxyl group (δ 3.60, m).

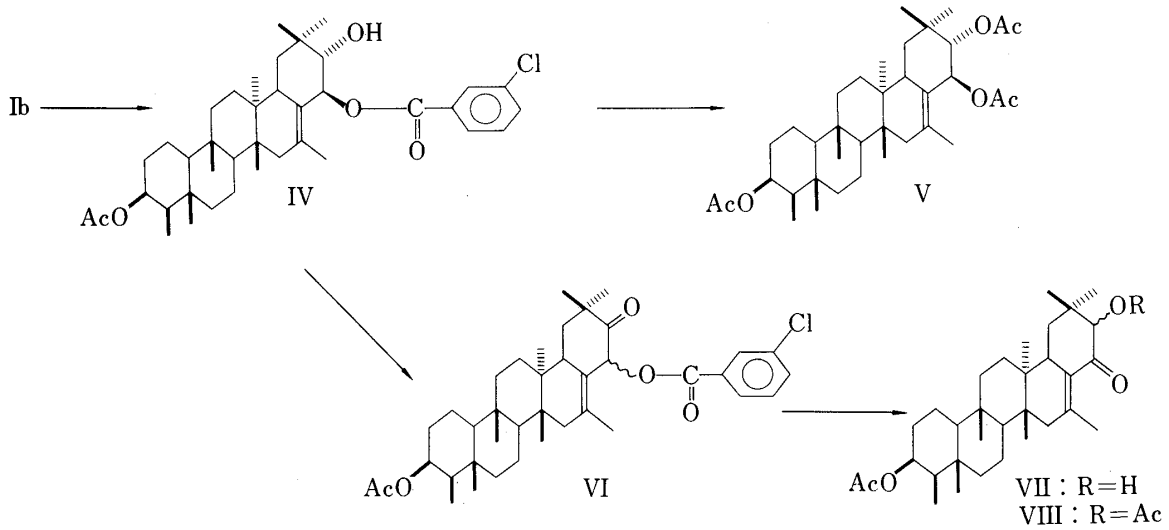


Chart 3

Lithium aluminum hydride reduction of IV, followed by acetylation, gave a triacetate (V). Its NMR spectrum shows a pair of doublets at δ 5.76 and 4.77 (each 1H, J=3 Hz, AcO–C<u>H</u>–C<u>H</u>–OAc), indicating that the two methine protons, and therefore two acetoxyl groups, are vicinal to one another.

On the other hand, oxidation of IV with CrO_3–AcOH afforded a ketone (VI), $C_{39}H_{53}ClO_5$, mp 211—213°C. Its UV spectrum exhibits an absorption maximum at 232 nm (ε: 12800), and its IR spectrum shows an absorption band at 1718 cm^{-1}, corresponding to a six-membered or larger ring ketone or an ester. Its NMR spectrum reveals that the proton geminal to the *m*-chlorobenzoyloxy group resonates at lower field (δ 6.18) than that of IV. Treatment of VI with methanolic $NaHCO_3$ gave a ketol (VII), $C_{32}H_{50}O_4$, mp 243—246°C, which was acetylated to afford a ketol acetate (VIII), $C_{34}H_{52}O_5$, mp 170—175°C. The IR spectrum of VIII exhibits conjugated ketone absorptions (1685 and 1610 cm^{-1}) and its UV spectrum shows the presence of an S-*cis*-α,β-unsaturated ketone system (257 nm; ε, 9870).[6] The NMR spectra of VII and VIII indicate the presence of a secondary alcohol in VII (VII: δ 3.75, br d, J=3 Hz, changes to rb s on addition of D_2O, C<u>H</u>–OH; VIII: δ 4.94, s, C<u>H</u>–OAc) and reveal a significant low field shift of the vinyl methyl signal (δ 1.87 in VII and δ 1.80 in VIII) in comparison with that of VI (δ 1.60), which is consistent with the S-*cis*-α,β-unsaturated ketone system in VII and VIII. It is considered that the ketone (VI) was partially hydrolyzed and concurrently isomerized to give the conjugated ketone (VII).

The above sequence of reactions provide chemical evidence in support of the diene system A in Ib.

Next, INDOR experiments were done with pachysandienol-B acetate (IIb) (see Fig. 2). Monitoring the olefinic protons at δ 5.62 gave an NOE peak at δ 1.73 (vinyl methyl) together with INDOR signals at around δ 1.95 (C_{21}–H_2) and around δ 2.51 (C_{18}–H). In turn, monitoring the olefinic proton at δ 5.70 afforded INDOR signals at δ 1.73, due to allylic coupling (J=2 Hz). In addition, monitoring the signal of hydrogen geminal to the acetoxyl group gave two NOE peaks at around δ 0.83, indicating that *sec*-methyl (δ 0.83) is located near the acetoxyl group.

Based on these observations, spin decoupling and NOE measurements were made. As shown in Fig. 3, the higher olefinic proton multiplet (δ 5.62) changed to a triplet (J=3.5 Hz)

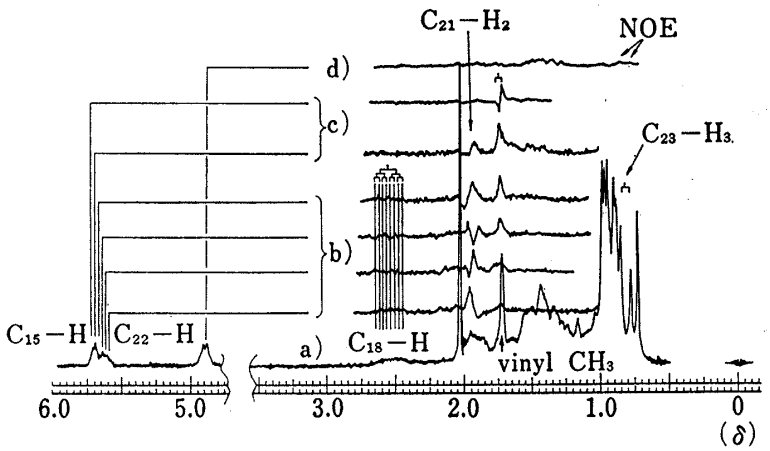


Fig. 2. INDOR Experiments with Pachysandienol-B Acetate (IIb)

a) 100 MHz NMR spectrum of IIb, b) INDOR spectra using the C_{23}–H signals as monitor lines ($J_{18-22}=2$ Hz, $J_{18-19}=5, 12$ Hz), c) INDOR spectra using the C_{15}–H signals as monitor lines ($J_{15-26}=2$ Hz), d) INDOR spectrum using the C_3–H signal as a monitor line.

on irradiation at δ 2.51 (C_{18}–H), and to a broad doublet ($J=2$ Hz) on irradiation at δ 1.95 (C_{21}–H_2) (Fig. 3b). Irradiation at δ 1.73 (vinyl methyl) caused sharpening of the lower-field olefinic proton singlet (δ 5.70), and concurrently gave a 15% NOE increase in the region of two olefinic proton resonances as shown in Fig. 3c.

From the above results, it is considered that pachysandienol-B acetate (IIb) has the partial structure B as shown in Chart 4.

Next, we carried out the catalytic hydrogenation of pachysandienol-A acetate (Ib) over Pd–C, which gave a 1,2-dihydro product (IX), $C_{32}H_{52}O_2$, mp 236—237°C, δ 1.59 (3H, s, vinyl CH_3), and a 1,4-dihydro product (X), $C_{32}H_{52}O_2$, mp 261—262°C, δ 5.35 (1H, m, olefinic H) and 1.02 (3H, d, $J=8$ Hz, *sec*-CH_3), in a ratio of 8: 1.

Pachysandienol-B acetate (IIb) was also hydrogenated over Pd–C to afford solely the dihydro compound IX, mp 237.5—238.5°C ,as shown in Chart 5.

The above dihydro products (IX and X) were found to be identical with 3β-acetoxy-28-nor-16-methyl-friedel-16-ene (IX) and 3β-acetoxy-28-nor-16β-methyl-friedel-17(22)-ene (X), which had been obtained in the MsCl treatment of 3-O-acetyl-pachysandiol-B (XIa),[1] respec-

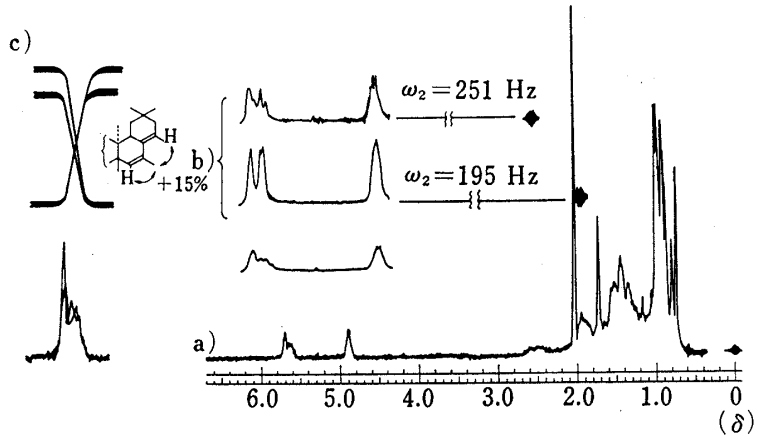
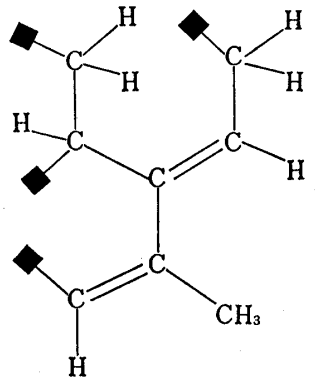


Fig. 3. Nuclear Magnetic Double Resonance Experiments with Pachysandienol-B Acetate (IIb)

a) 100 MHz NMR spectrum of IIb, b) spin decou pling, c) measurement of NOE between vinyl methyl and olefinic proton (irr. at δ 1.73).



B

Chart 4

tively, by gas chromatography (GC), IR (KBr), and NMR comparisons. Accordingly, the structures of pachysandienol-A and -B were established to be Ia and IIa, respectively. Apparently pachysandienol-A (Ia) and -B (IIa) are the first examples of the 28-nor-16-methyl-friedelane series[7] among natural products.

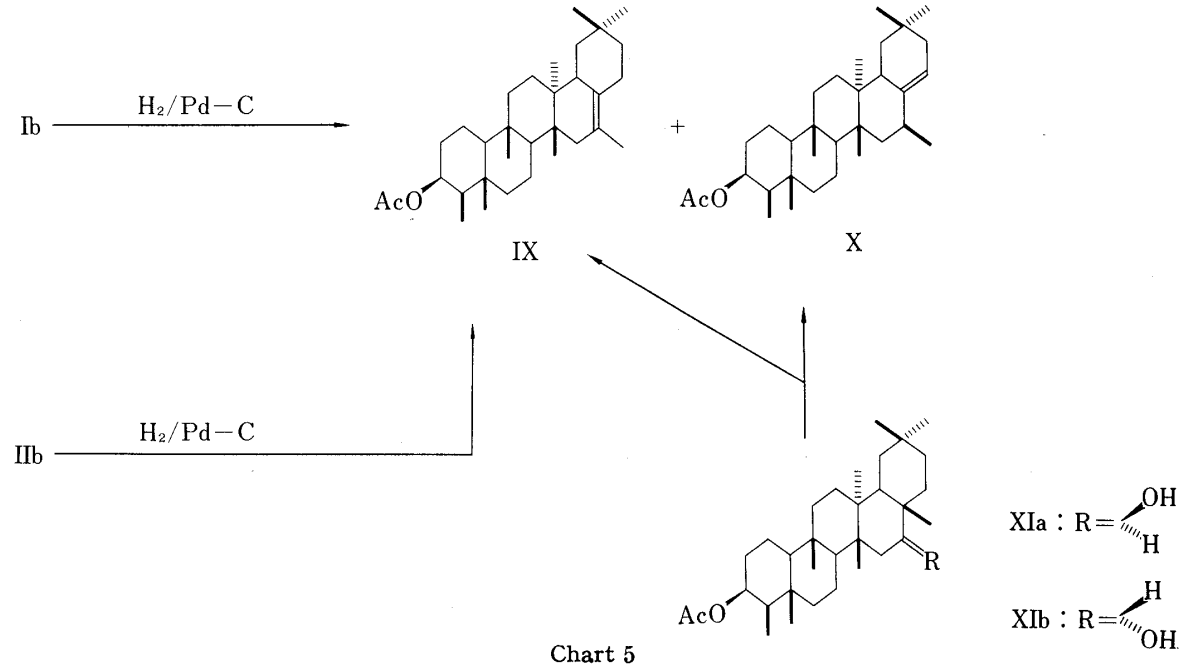


Chart 5

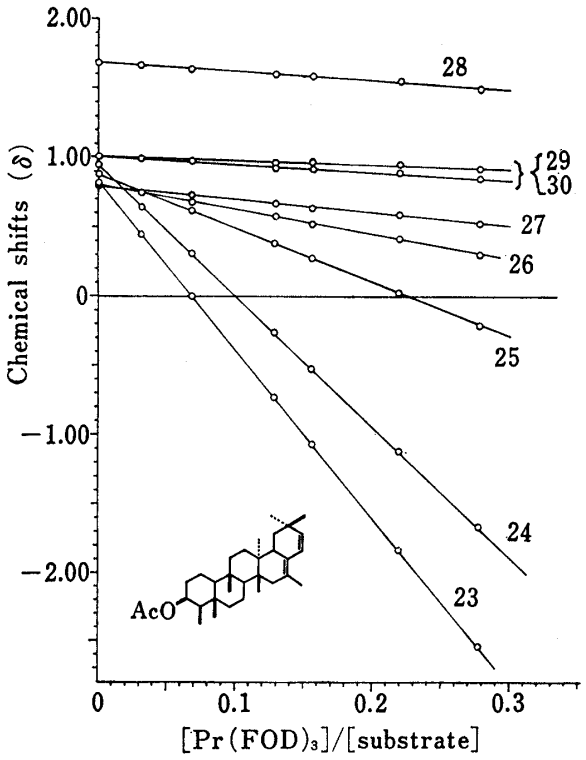


Fig. 4. Lanthanide-induced Shifts of Methyl Signals of Pachysandienol-A Acetate (Ib), plotted against the Molar Ratios of $Pr(FOD)_3$ to Substrate

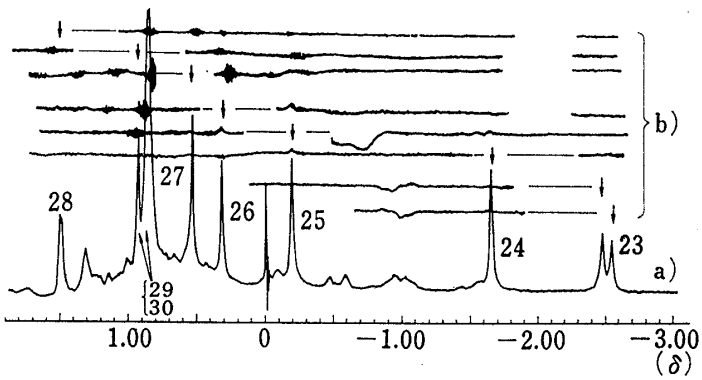


Fig. 5. INDOR Experiments with Pachysandienol-A Acetate (Ib)

a) 100 MHz NMR spectrum of Ib in the presence of $Pr(FOD)_3$, b) INDOR spectra.

Last, the methyl resonances of pachysandienol-A acetate (Ib) and pachysandienol-B acetate (IIb) were assigned by using the INDOR method in combination with the pseudo-contact shift in the same way as was applied to friedelin and its derivatives.[3] The lanthanide-induced shift patterns of methyl resonances of Ib and IIb (see Fig. 4 and Fig. 6) were very similar to that of epifriedelanol acetate[3] and NOE's between 23- and 24-methyls, 24- and 25-methyls, and 25- and 26-methyls were observed by the use of the INDOR method, as shown in Fig. 5 and Fig. 7. These observations led to assignments of the methyl resonances of Ib and IIb as shown in Table I.

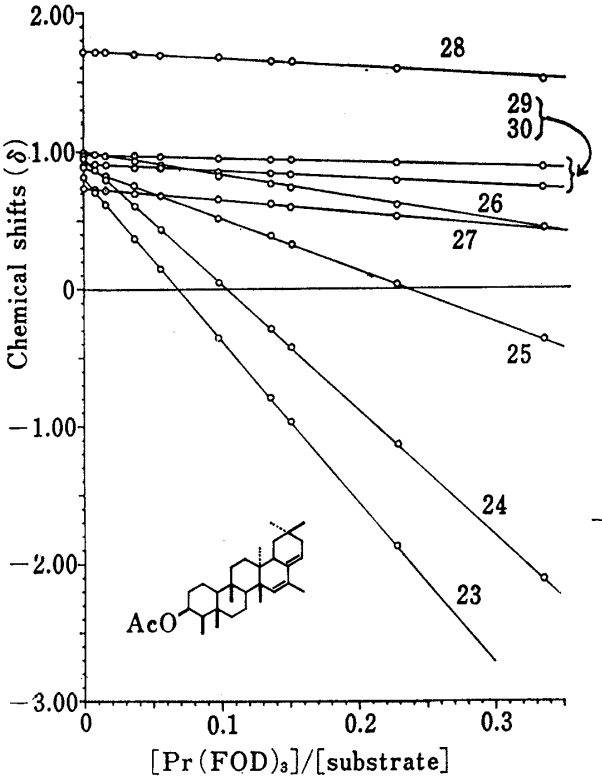


Fig. 6. Lanthanide-induced Shifts of Methyl Signals of Pachysandienol-B Acetate (IIb), plotted against the Molar Ratios of Pr $(FOD)_3$ to Substrate

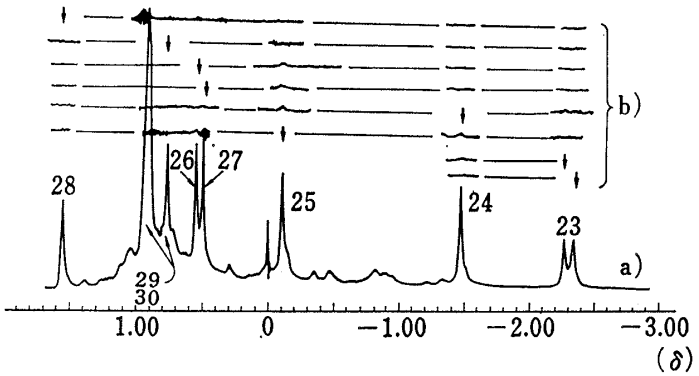


Fig. 7. INDOR Experiments with Pachysandienol-B Acetate (IIb)

a) 100 MHz NMR spectrum of IIb in the presence of $Pr(FOD)_3$, b) INDOR spectra.

Table I. Assignments of Methyl Resona nces of Pachysandienol-A Acetate (Ib) and Pachysandienol-B Acetate (IIb)

	23	24	25	26	27	28	29, 30
Pachysandienol-A acetate (Ib)	δ 0.83	0.95	0.88	0.80	0.80	1.68	{1.02 1.02
Pachysandienol-B acetate (IIb)	0.83	0.95	0.89	0.99	0.73	1.72	{0.91 0.97

Experimental

Melting points were determined with a Kofler-type apparatus and are uncorrected. All specific rotations were measured in chloroform solutions. Mass spectral (MS) determination were performed with a Hitachi RMU-6D mass spectrometer with a direct inlet system and high resolution MS measurements were made with a JEOL JMS-D300 instrument. Infrared (IR) spectra were measured on a Hitachi KPI spectrometer for chloroform solutions, unless otherwise noted. Usual NMR measurements were made for deuteriochloroform solutions with a Varian A-60 spectrometer and chemical shifts are given in the δ-scale with reference to

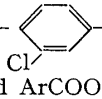
tetramethylsilane as an internal standard. NMR measurements in the presence of NMR shift reagent were made after adding a weighed amount of the reagent to a solution of the substrate in $CDCl_3$. INDOR spectra were measured with a Varian HA-100D instrument modified for INDOR experiments. Preparative thin-layer chromatography (TLC) was performed on Merck Kieselgel GF_{254} with chloroform or methanol–chloroform mixture and plates were examined under ultraviolet light. Preparative $AgNO_3$–TLC was carried out on $AgNO_3$-impregnated Kieselgel with chloroform and detection of substances was achieved by spraying water. For extraction of substances from the Kieselgel, methylene chloride or methylene chloride–methanol mixture was used as a solvent. For drying organic solutions, anhydrous $MgSO_4$ was employed.

Pachysandienol-A Acetate (Ib)——Pachysandienol-A acetate (Ib) was obtained as colorless needles, mp 260—261°C, after recrystallization from CH_2Cl_2–MeOH. $[\alpha]_D^{28}$ +194.0° (c=0.89). MS m/z: 466 (M^+). *Anal.* Calcd for $C_{32}H_{50}O_2$: C, 82.34; H, 10.80. Found: C, 82.11; H, 10.52. IR ν_{max} cm^{-1}: 1720, 1260 (OAc). UV λ_{max}^{EtOH} nm: 240 (sh), 245 (ε: 24400), 252 (sh). NMR δ: 6.25, 5.39 (each 1H, d, J=10 Hz, $_H\rangle C{=}C\langle_H$), 4.90 (1H, m, C<u>H</u>–OAc), 2.03 (3H, s, Ac), 1.68 (3H, d, J=1 Hz, vinyl CH_3: changed to s on irradiation at δ 2.15), 1.02—0.79 (6×*tert*-CH_3), 0.82 (3H, d, J=6 Hz, *sec*-CH_3).

Pachysandienol-A (Ia)——A mixture of pachysandienol-A acetate (Ib) (50 mg), 10% KOH in MeOH (7 ml), and benzene (3 ml) was refluxed for 5 h. The reaction mixture was concentrated *in vacuo*, diluted with water, and extracted with ether. The ether extract was washed with water, dried, and concentrated to give a crystalline residue (40 mg). The residue was purified by preparative $AgNO_3$–TLC, followed by recrystallization from ether–MeOH, to afford colorless needles (Ia) (20 mg), mp 211—213°C. $[\alpha]_D^{28}$ +153.1° (c=1.12). MS m/z: 424 (M^+). *Anal.* Calcd for $C_{30}H_{48}O$: C, 84.84; H, 11.39. Found: C, 84.95; H, 11.62. NMR δ: 6.28, 5.40 (each 1H, d, J=10 Hz, $_H\rangle C{=}C\langle_H$), 3.74 (1H, br, C<u>H</u>–OH), 1.69 (3H, d, J=1 Hz, vinyl CH_3), 1.01—0.78 (7×CH_3). IR ν_{max} cm^{-1}: 3600 (OH).

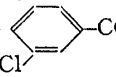
Pachysandienol-B Acetate (IIb)——Pachysandienol-B acetate (IIb) was obtained as colorless needles, mp 228—229°C, after recrystallization from CH_2Cl_2–MeOH. $[\alpha]_D^{13}$ +76.4° (c=0.79). MS m/z: 466 (M^+). *Anal.* Calcd for $C_{32}H_{50}O_2$: C, 82.34; H, 10.80. Found: C, 82.17; H, 10.97. IR ν_{max} cm^{-1}: 1720, 1255 (OAc). UV λ_{max}^{EtOH} nm: 239 (sh), 246 (ε: 17700), 253 (sh). NMR δ: 5.70 (1H, br s, olefinic H), 5.62 (1H, m, olefinic H), 4.90 (1H, br, $W_{h/2}$=6.5 Hz, C<u>H</u>–OAc), 2.03 (3H, s, Ac), 1.73 (3H, d, J=1.5 Hz, vinyl CH_3), 1.00—0.74 (7×CH_3).

Pachysandienol-B (IIa)——Pachysandienol-B acetate (IIb) (42 mg) was stirred with excess $LiAlH_4$ (100 mg) in dry ether (10 ml) under reflux for 6 h. Usual work-up of the reaction mixture and subsequent recrystallization from ether–MeOH afforded pachysandienol-B (IIa) (15 mg), colorless needles, mp 236—241 °C. $[\alpha]_D^{23}$ +89.5° (c=0.94). MS m/z: 424 (M^+). *Anal.* Calcd for $C_{30}H_{48}O\cdot H_2O$: C, 81.39; H, 11.38. Found: C, 81.86; H, 11.60. UV λ_{max}^{EtOH} nm: 240 (sh), 247 (ε: 15300), 254 (sh). IR ν_{max} cm^{-1}: 3600 (OH). NMR δ: 5.68 (2H, br, olefinic H), 3.75 (1H, br, $W_{h/2}$=6.5 Hz, C<u>H</u>–OH), 1.70 (3H, br s, vinyl CH_3), 0.99—0.72 (6×*tert*-CH_3), 0.83 (3H, d, J=6.5 Hz, *sec*-CH_3).

Reaction of Pachysandienol-A Acetate (Ib) with *m*-Chloroperbenzoic Acid——A solution of pachysandienol-A acetate (Ib) (31 mg) in abs. benzene (5 ml) was treated with *m*-chloroperbenzoic acid (14 mg) and the reaction mixture was left to stand overnight in the dark at room temperature. Excess *m*-chloroperbenzoic acid was destroyed by addition of aqueous sodium sulfite and the mixture was extracted with ether. The ether solution was washed with dil. Na_2CO_3, dried, and concentrated *in vacuo*. The oily residue (37 mg) was subjected to preparative TLC to afford a crystalline residue (27 mg) which was recrystallized from ether–MeOH to give an *m*-chlorobenzoyloxy-alcohol (IV) (20 mg), colorless leaves, mp 145—147°C. $[\alpha]_D^{25}$ +63.6° (c=1.0). *Anal.* Calcd for $C_{39}H_{55}ClO_5\cdot 1/2H_2O$: C, 72.25; H, 8.70. Found: C, 72.50; H, 8.85. MS m/z: 482 (M^+—  –CO_2H). UV λ_{max}^{EtOH} nm: 232 (ε: 10820). IR ν_{max} cm^{-1}: 3600, 3500 (OH), 1720, 1580, 1255 (AcO and ArCOO). NMR δ: 8.00—7.30 (4H, aromatic protons), 6.07 (1H, d, J=3 Hz, C<u>H</u>–OCOAr), 4.90 (1H, br, $W_{h/2}$=6.5 Hz, C<u>H</u>–OAc), 3.60 (1H, m, C<u>H</u>–OH), 2.03 (3H, s, Ac), 1.73 (3H, d, J=1 Hz, vinyl CH_3), 1.14—0.80 (7×CH_3).

Lithium Aluminum Hydride Reduction of the *m*-Chlorobenzoyloxy-alcohol (IV) and Subsequent Acetylation——$LiAlH_4$ (50 mg) was added to a solution of the above compound IV (15 mg) in dry ether (5 ml) and the mixture was stirred at room temperature for 2 h. The reaction mixture was poured into water and the product was taken up in ether. The ether solution was washed successively with 3% HCl, dil. Na_2CO_3, and water, dried, and concentrated to give a crystalline residue (12 mg). Recrystallization of this residue from ether–hexane gave a triol (11 mg), colorless prisms, mp 250—255°C. High resolution MS m/z: Found 458.3766 (M^+). Calcd for $C_{30}H_{50}O$=458.3760.

The above triol (10 mg) was mixed with acetic anhydride–pyridine (each 0.5 ml) and left to stand overnight at room temperature. The reaction mixture was worked up in the usual manner to give a crystalline residue (13 mg), which was purified by preparative TLC and subsequent recrystallization from CH_2Cl_2–MeOH to afford a triacetate (V) (6 mg), colorless needles, mp 156—160°C. MS m/z: 542 (M^+—42). IR ν_{max} cm^{-1}: 1725, 1250 (OAc). NMR δ: 5.76 (1H, br d, J=3 Hz, C<u>H</u>–OAc), 4.90 (1H, br, $W_{h/2}$=6 Hz, C<u>H</u>–OAc), 4.77 (1H, br d, J=3 Hz, C<u>H</u>–OAc), 2.03 (6H, s, 2×Ac), 1.99 (3H, s, Ac), 1.64 (2H, d, J=1 Hz, vinyl CH_3), 1.13—0.73 (7×CH_3).

Chromium Trioxide Oxidation of the *m*-Chlorobenzoyloxy-alcohol (IV)——A mixture of compound IV (17 mg), benzene (2 ml), AcOH (2 ml), and CrO_3 (10 mg) was stirred for 40 min at room temperature. The reaction mixture was diluted with water, and extracted with ether. The organic layer was washed with dil. Na_2CO_3, dried, and concentrated to afford an oily residue, which crystallized on addition of MeOH. Recrystallization from ether–MeOH gave a ketone (VI) (12 mg), colorless needles, mp 211—213°C. $[\alpha]_D^{24}$ +41.8° (c=1.0). MS m/z: 480 ($M^+ -$  $-CO_2H$). *Anal.* Calcd for $C_{39}H_{53}ClO_5$: C, 73.50; H, 8.38; O, 12.55. Found: C, 73.79; H, 8.53; O, 12.63. UV λ_{max}^{EtOH} nm: 232 (ε: 12800). IR ν_{max} cm^{-1}: 1718, 1575, 1253 (six-membered ring ketone, AcO, and ArCOO). NMR δ: 8.05—7.30 (4H, aromatic protons), 6.18 (1H, br, C<u>H</u>–OCOAr), 4.90 (1H, br, C<u>H</u>–OAc), 2.03 (3H, s, Ac), 1.60 (3H, br s, vinyl CH_3), 1.23—0.83 (7×CH_3).

Partial Hydrolysis of the Keto-*m*-chlorobenzoate (VI)——A solution of the keto-*m*-chlorobenzoate (VI) (34 mg) in 10% $NaHCO_3$ (1 ml) and MeOH (9 ml) was refluxed for 4 h and then the whole was left to stand overnight at room temperature. The mixture was concentrated *in vacuo*, diluted with water, and extracted with ether. The ether solution was washed with dil. Na_2CO_3, dried, and concentrated to give a crystalline residue (20 mg). Preparative TLC and subsequent recrystallization from CH_2Cl_2–MeOH gave a pure ketol (VII) (13 mg), mp 243—246°C. High resolution MS m/z: Found 498.3714 (M^+). Calcd for $C_{32}H_{50}O_4$= 498.3709. IR ν_{max} cm^{-1}: 3400 (OH), 1715, 1250 (AcO), 1670, 1610 (C=C–C=O). NMR δ: 4.90 (1H, br, C<u>H</u>–OAc), 3.95 (1H, d, J=3 Hz, CH–O<u>H</u>; disappears on addition of D_2O), 3.75 (1H, br d, J=3 Hz, C<u>H</u>–OH; changes to br s on addition of D_2O), 2.03 (3H, s, Ac), 1.87 (3H, d, J=1 Hz, vinyl CH_3), 0.96—0 80 (7×CH_3).

Acetylation of the Ketol (VII)——A mixture of the ketol (VII) (28 mg), acetic anhydride (0.5 ml), and pyridine (0.5 ml) was left to stand for 2 d at room temperature. Usual work-up of the reaction mixture and preparative TLC gave a crystalline residue (13 mg), which was recrystallized from CH_2Cl_2–MeOH to afford a ketol acetate (VIII) (10 mg), colorless needles, mp 170—175°C. MS m/z: 540 (M^+, $C_{34}H_{52}O_5$). UV λ_{max}^{EtOH} nm: 257 (ε: 9870). IR ν_{max} cm^{-1}: 1720, 1250 (OAc), 1685, 1610 (C=C–C=O). NMR δ: 4.94 (1H, s, C<u>H</u>–OAc), 4.90 (1H, br, C<u>H</u>–OAc), 2.20 (3H, s, Ac), 2.03 (3H, s, Ac), 1.80 (3H, d, J=1 Hz, vinyl CH_3), 1.06—0.77 (7×CH_3).

Catalytic Hydrogenation of Pachysandienol-A Acetate (Ib)——Pachysandienol-A acetate (Ib) (115 mg) was hydrogenated over 5% Pd-C (120 mg) in AcOEt (15 ml) and MeOH (5 ml) at room temperature and atmospheric pressure for 48 h. The catalyst was filtered off and the filtrate was concentrated *in vacuo* to afford a crystalline residue (110 mg, roughly 4: 1 mixture of IX and X), which was chromatographed on silica gel (50 g) using benzene–hexane (15: 85 and 30: 70). The less polar fraction was repeatedly chromatographed on silica gel and then recrystallized from ether–MeOH to give the 1,2-dihydro product (IX) (30 mg), colorless needles, mp 236—237°C. $[\alpha]_D^{23}$ +63.9° (c=0.76). MS m/z: 468 (M^+). *Anal.* Calcd for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18. Found: C, 82.21; H, 11.53. IR ν_{max} cm^{-1}: 1720, 1250 (OAc). NMR δ: 4.90 (1H, m, C<u>H</u>–OAc), 2.04 (3H, s, Ac), 1.57 (3H, br s, J=2 Hz, vinyl CH_3), 0.92—0.75 (7×CH_3). Physical data for this product were identical with those of 3β-acetoxy-28-nor-16-methyl-friedel-16-ene (IX) obtained by the MsCl-dehydration of 3-O-acetyl-pachysandiol-B.[1)]

On the other hand, the more polar fraction (*ca.* 50 mg) was treated with ether to afford a fairly poorly soluble substance. This was collected and recrystallized from ether–MeOH to give the 1,4-dihydro product (X) (7 mg), colorless prisms, mp 260—261°C. $[\alpha]_D^{24}$ +45.6° (c=0.94). MS m/z: 468 (M^+, $C_{32}H_{52}O_2$). IR ν_{max} cm^{-1}: 1720, 1260 (OAc). NMR δ: 5.35 (1H, m, olefinic H), 4.90 (1H, m, C<u>H</u>–OAc), 2.04 (3H, s, Ac), 1.02—0.76 (8×CH_3). This product was identical with 3β-acetoxy-28-nor-16β-methyl-friedel-17(22)-ene (X) derived from 3-O-acetyl-16-epi-pachysandiol-B.[1)]

Catalytic Hydrogenation of Pachysandienol-B Acetate (IIb)——Pachysandienol-B acetate (IIb) (30 mg) was hydrogenated over 5% Pd-C (100 mg) in AcOEt (5 ml) and MeOH (3 ml) at room temperature and atmospheric pressure. The catalyst was filtered off and the filtrate was concentrated under reduced pressure. The crystalline residue (27 mg) thereby obtained was recrystallized from CH_2Cl_2–MeOH to afford a dihydro product (23 mg), colorless needles, mp 237.5—238.5°C. $[\alpha]_D^{19}$ +62.6° (c=1.17). IR ν_{max} cm^{-1}: 1720, 1255 (OAc). NMR δ: 4.90 (1H, br, $W_{h/2}$=6 Hz, C<u>H</u>–OAc), 2.03 (3H, s, Ac), 1.57 (3H, br s, J=2 Hz, vinyl CH_3), 0.94—0.75 (7×CH_3). The IR(KBr) and NMR spectra of this sample were identical with those of the 1,2-dihydro product (IX) obtained from pachysandienol-A acetate (Ib).

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References and Notes

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6) A.I. Scott, "Interpretation of the UV Spectra of Natural Products," Pergamon Press, London, 1964, p. 58.
7) At present, however, we cannot completely exclude the possibility that Ia and IIa might have been derived from friedelane derivatives having a hydroxyl group or its equivalent at the C_{16}-position during the extraction process, since 28-nor-16-methyl-friedelanes are readily obtained by treatment of 3-O-acetyl-pachysandiol-B (XIa) and 3-O-acetyl-16-epi-pachysandiol-B (XIb) with methanesulfonyl chloride.[1] As yet we have not found any compound that we consider to be a precursor of Ia and IIa. This problem is still under investigation.