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Studies on the Neutral Constituents of *Pachysandra terminalis* Sieb et Zucc. III.[1] Structure of Pachysandiol-A and a Note on the Stereochemistry of Cerin[2]

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The structure of pachysandiol-A, a new triterpenediol isolated from the neutral fraction of *Pachysandra terminalis* Sieb. et Zucc. (Buxaceae), was investigated and assigned to the formula I on the basis of chemical and spectroscopic evidences. In this connection, the 2-hydroxyl group of cerin, for which 2β (equatorial)-orientation had been proposed, was proved to have the axial 2α-configuration.

In preceding papers[1,4] we reported the isolation and characterization of several kinds of sterols, friedelin-type triterpenoids, and cycloartenol-type triterpenoids from the benzene-soluble, neutral fraction obtained by alkaline hydrolysis of the neutral components of *Pachysandra terminalis* Sieb. et Zucc. (Japanese name: Fukki-so), a Buxaceae plant. This paper deals with the full detail of structure elucidation of a new triterpenediol, for which we proposed the name pachysandiol-A.[2]

Pachysandiol-A (I) was first isolated as its diacetate (IIa),[4] mp 235—236°, and the lithium aluminum hydride reduction of the latter gave a pure diol (I), mp 291—292°, $[\alpha]_D$ +14° ($CHCl_3$). It was analysed for $C_{30}H_{52}O_2$ which is in agreement with the molecular ion peak at *m/e* 444 in the mass spectrum,[5] and shows a strong hydroxyl absorption in the infrared (IR) spectrum[6] and the positive Liebermann–Burchard color reaction.

The presence of two secondary hydroxyl groups in pachysandiol-A (I) was suggested by the inspection of the nuclear magnetic resonance (NMR) spectrum[7] (Fig. 1) of its diacetate (IIa) which exhibits the signals for two acetyl groups and two hydrogens geminal to the acetoxyl groups in addition to a secondary methyl (9.18 τ, d, J=7 cps) and seven tertiary methyl groups.

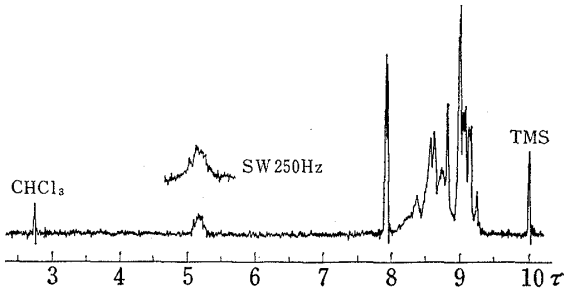

Fig. 1. NMR Spectrum of Pachysandiol-A diacetate

Upon periodic acid oxidation, it gave an aldehyde as proved by the IR bands at 1717 and 2750 cm^{-1} and by NMR signals at 0.15—0.30 τ, indicating that the two hydroxyl groups consist of an α-glycol system.

1) Part II: T. Kikuchi and M. Takayama, *Yakugaku Zasshi*, **90**, 1051 (1970).
2) Preliminary communication of this work appeared in *Tetrahedron Letters*, **1967**, 3181.
3) Location: *Yoshida-shimoadachi-cho, Sakyo-ku, Kyoto*; *a*) Present address: *Shionogi Research Laboratory, Shionogi & Co., Ltd., Fukushima-ku, Osaka.*
4) T. Kikuchi, T. Toyoda, M. Arimoto, M. Takayama, and M. Yamano, *Yakugaku Zasshi*, **89**, 1358 (1969).
5) Mass spectra were determined on a Hitachi Mass Spectrometer Model RMU-6D equipped with a direct inlet system (Model MG-150).
6) Infrared spectra were taken in chloroform solution unless otherwise specified.
7) All the NMR spectra were measured on a Varian Associates A-60 NMR Spectrometer (60 Mc) in deuterated chloroform solutions and chemical shifts are recorded in τ values using tetramethylsilane as the internal reference.

Of these two hydroxyl groups, remarkable difference was observed in the reactivity. When pachysandiol-A (I) was treated with acetic anhydride and pyridine at room temperature, there was obtained a monoacetate (IIb), $C_{32}H_{54}O_3$, mp 245—247°, $[\alpha]_D$ −4° ($CHCl_3$), accompanied by a small amount of an isomeric monoacetate (IIc), $C_{32}H_{54}O_3$, mp 291—292°, $[\alpha]_D$ +10° ($CHCl_3$). In accord with this observation, the latter was produced as the principal product in the selective reduction of the diacetate (IIa) with lithium aluminum hydride.

Chromium trioxide oxidation of the monoacetate IIb gave rise to a corresponding keto-acetate (IVa), $C_{32}H_{52}O_3$, mp 260—262°, as indicated by its IR bands at 1723 and 1738 cm^{-1}. The same oxidation on the other monoacetate IIc proceeded similarly to give an isomeric keto-acetate (Va), $C_{32}H_{52}O_3 \cdot H_2O$, mp 255—257°.

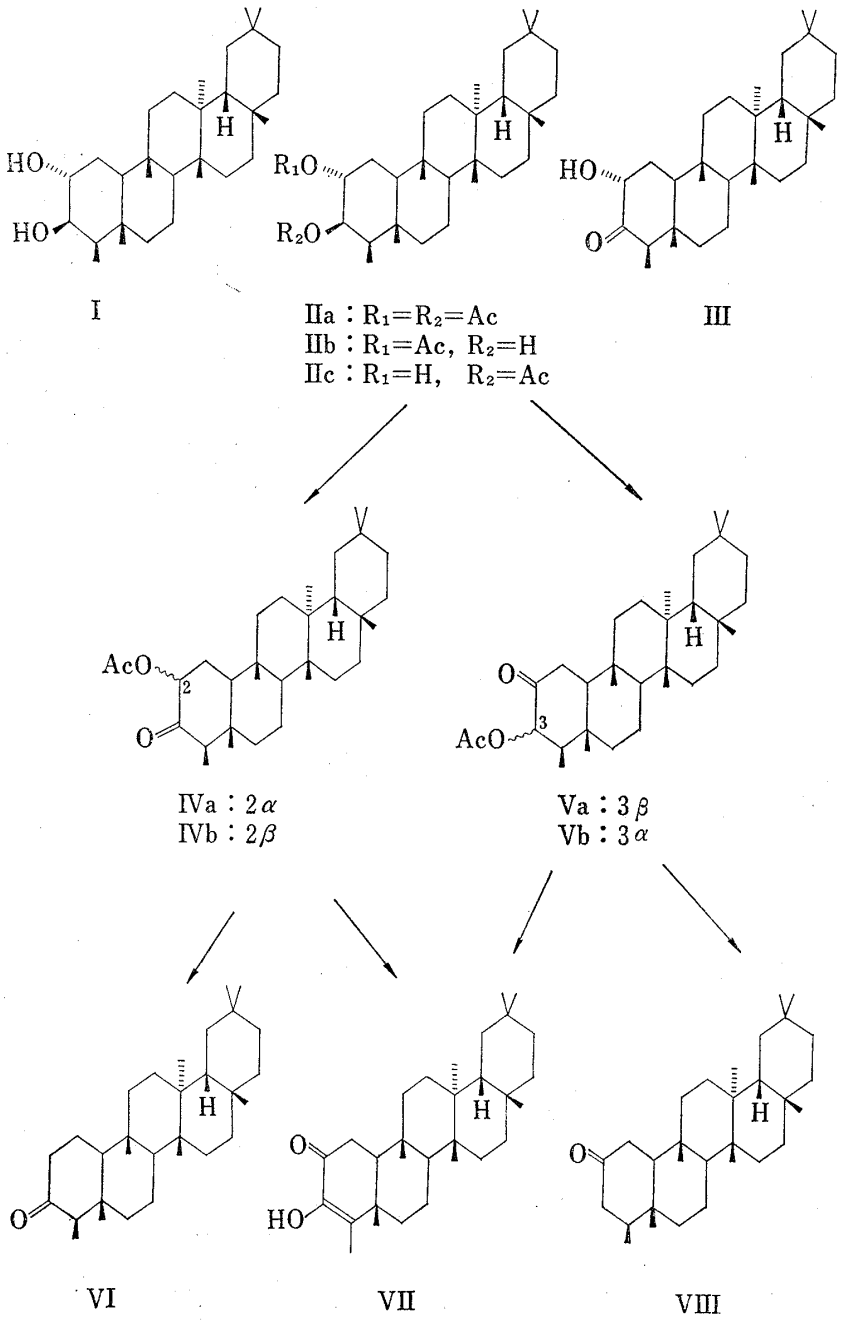

Chart 1

When the keto–acetate (IVa) was treated with zinc in boiling acetic acid, elimination of the acetoxyl group occurred easily,[8] confirming the vicinal disposition of the two oxygen functions. The ketone thereby obtained, mp 259—260°, was found to be identical with friedelin (VI) in all respects. Furthermore, mild alkaline hydrolysis of this keto–acetate (IVa) followed by oxidation with bismuth trioxide[9] afforded 3-hydroxyfriedel-3-en-2-one (VII), mp 270—273°, $[\alpha]_D$ +29° ($CHCl_3$), which shows the characteristic IR bands at 3460, 1668, and 1640 cm^{-1}, UV maximum (in dioxane) at 275 mμ (ε 9650), and NMR signal for the newly formed vinyl methyl group at 8.18 τ (3H, s). The identity was established by direct comparison with an authentic sample.[10,11]

The isomeric keto-acetate (Va) also yielded 3-hydroxyfriedel-3-en-2-one (VII) upon hydrolysis with potassium hydroxide in boiling methanol.[12] On the other hand, reduction of the compound Va with zinc in acetic acid proceeded easily to give a ketone (VIII), mp 287—288°, $[\alpha]_D$ −7° ($CHCl_3$), ν_{max} 1700 cm^{-1}, whose physical constants are in excellent agreement with the reported values of friedel-2-one (VIII).[10]

From the foregoing results, pachysandiol-A must be 2,3-dihydroxyfriedelane.

Table I

Compound	2-H(τ)	3-H(τ)	23-Me(τ)	24-Me(τ)
Pachysandiol-A diacetate (IIa)	5.15 (m) $W^{1/2}$ about 9 cps	5.15 (m)	9.19 (d) J=7 cps	9.09 (s)
Pachysandiol-A 2-acetate (IIb)	5.05 (q) J=3 cps	6.45 (br, t) J=3 cps	9.08 (d) J=7 cps	9.00 (s) (or 9.05)
Pachysandiol-A 3-acetate (IIc)	6.09 (m) $W^{1/2}$ 7 cps	5.30 (t) J=3 cps	9.20 (d) J=7 cps	9.09 (s)

Table II

Compound	NMR (C<u>H</u>-OAc)	UV λ_{max} (in dioxane)	ORD (Cotton effect in dioxane)		
			Sign	Peak	Trough
Keto-acetate IVa	5.05τ(t) J=2.5 cps	295 mμ	−	$[\phi]_{279}$+1350	$[\phi]_{324}$−3100
Keto-acetate IVb	4.81τ(q) J=6, 11 cps	287 mμ	−	$[\phi]_{269}$+5040	$[\phi]_{307}$−6500
Friedelin (VI)		288 mμ	−	$[\phi]_{262}$+6220	$[\phi]_{314}$−5620
Keto-acetate Va	5.00τ(d) J=4 cps	295 mμ	+	$[\phi]_{324}$+2900	$[\phi]_{280}$−1650
Keto-acetate Vb	5.05τ(d) J=12 cps	277 mμ	−	$[\phi]_{265}$+2710	$[\phi]_{307}$−3390
Friedelan-2-one (VIII)		276 mμ	−	$[\phi]_{270}$+1340	$[\phi]_{311}$−1000

Turning to the stereochemistry at 2- and 3-positions, the 2α,3β-configuration was first suggested by the inspection of NMR spectra of pachysandiol-A diacetate (IIa) and two monoacetates (IIb and IIc).

The NMR spectra of a series of friedelin derivatives have been studied by Takahashi, *et al.*[13] who reported that the C_{24}-protons of friedelane resonate at 9.25 τ while those of epifriedelanol and its acetate with the 3β-configuration at 9.00 and 9.05 τ, respectively. In the case of IIa, IIb, and IIc, the NMR signals attributable to the C_{24}-protons appear at 9.09—

8) R. B. Woodward, F. Sondheimer, D. Taub, K. Heusler, and W. M. McLamore, *J. Am. Chem. Soc.*, **74**, 4225 (1952).
9) W. Rigby, *J. Chem. Soc.*, **1951**, 793.
10) E. J. Corey and J. J. Ursprung, *J. Am. Chem. Soc.*, **78**, 5041 (1956).
11) V. V. Kane and R. Stevenson, *J. Org. Chem.*, **25**, 1394 (1960).
12) The formation of VII may be due to the air oxidation of an initially produced keto-alcohol during the alkaline hydrolysis.
13) T. Takahashi, *Nippon Kagaku Zasshi*, **87**, 101 (1966).

9.00 τ region as shown in Table I, reflecting the 1,3-diaxial relationship between the C_3-oxygen functions and C_5-methyl groups. Moreover, the splitting pattern of C_2- and C_3-hydrogens (Table I) indicates the equatorial disposition of these hydrogens.[14]

Confirmative evidences were advanced as follows. When the keto-acetate IVa was adsorbed onto alumina[15] overnight and then eluted with benzene–chloroform, there was obtained an epimer (IVb), $C_{32}H_{52}O_3$, mp 226—228°, $[\alpha]_D$ −55° ($CHCl_3$). Like the compound IVa, the latter could be transformed to friedelin (VI) by the zinc-acetic acid reduction albeit the reaction proceeded in fairly slow rate [16] and also to 3-hydroxyfriedel-3-en-2-one (VII) in the same manner as run with IVa. In the NMR spectrum of IVb the signal of the hydrogen geminal to the acetoxyl group appears at 4.81 τ as a quartet with the large coupling constants in contrast to the small values of the corresponding hydrogen in IVa (Table II).[14]

These observations led to the assignment of axial 2α-configuration to the less stable keto-acetate (IVa) and equatorial 2β-orientation to the more stable epimer (IVb).

In support for this conclusion the ultraviolet (UV) absorption maximum and the first extreme of the Cotton effect in optical rotatory dispersion (ORD) curve of the former compound (IVa) occur at about 17 mμ longer wavelength than those of the latter (IVb) (Table II).[17]

On the other hand, the keto-acetate Va isomerized readily on alumina chromatography[15] to yield a compound (Vb), mp 270—272°, $[\alpha]_D$ −55° ($CHCl_3$). This compound could be formulated in term of the 3-epimer (Vb), since it gave rise to the same ketone (VIII) as obtained from Va upon treatment with zinc in boiling acetic acid. However, the rate of this reductive cleavage was relatively slow, suggesting the equatorial orientation of the acetoxyl group.[16] In addition, the spectroscopic behavior as shown in Table II indicates evidently the equatorial 3α-configuration in the compound Vb. Therefore the 3-acetoxyl group in the keto-acetate Va must have the β-orientation.

Of interest in this connection is the observation that the (ORD) curve of Va exhibits a positive Cotton effect with the peak at 324 mμ in contrary to the anticipation. This can be consistently explained if we assume the ring-A in Va has a twist form, which may become preferred due to the large 1,3-interaction between 3β-acetoxyl group and the 5β-methyl group in the alternative chair conformation.

On the basis of the above evidences, the structure of pachysandiol-A is unequivocally assigned to the formula I.[18]

It should be noted herewith that the structure of cerin has been proposed to be 2β-hydroxyfriedelin (III, with 2β-hydroxyl) by Corey, *et al.*[10] and by Ourisson, *et al.*[19] and hence cerin acetate to be IVb. In the present study, however, the keto-acetate IVa was found to be identical in every respect with the acetate sample, mp 259—262°, derived from authentic cerin. Therefore, the structure of cerin should be revised to the formula III with 2α-configuration.

Experimental[20]

Pachysandiol-A (I)——Pachysandiol-A diacetate (0.72 g) was reduced with excess $LiAlH_4$ (0.5 g) in boiling ether–tetrahydrofuran for 5 hr and worked up as usual. Recrystallizations of the product from

14) N. S. Bhacca and D. H. Williams, "Applications of NMR Spectroscopy in Org. Chem.," Holden-Day, Inc., San Francisco, 1964, p. 49.
15) Merck Aluminum oxide standardized, activity I, was employed.
16) H. O. House, "Modern Synthetic Reactions," Benjamin, Inc., New York, 1965, p. 57.
17) C. Djerassi, "Optical Rotatory Dispersion," McGraw-Hill, Inc., New York, 1960, p. 111.
18) Recently it was reported by Stevenson, *et al.* that the compound I was obtained by two routes from friedelin and from cerin (see A. S. Samson, S. J. Stevenson, and R. Stevenson, *J. Chem. Soc.* (*C*), **1968**, 2342).
19) T. Takahashi and G. Ourisson, *Bull. Soc. Chim. France*, **1956**, 353. In Ourisson's later paper the structure of cerin was depicted as III, but no comment on this alteration appeared in hitherto published literature (see P. Witz, H. Herrmann, J. M. Lehn, and G. Ourisson, *Bull. Soc. Chim. France*, **1963**, 1101).
20) All the melting points were determined on a Yanagimoto Micro Melting Point Apparatus and are uncorrected. All the specific rotations were measured in chloroform solutions.

$CHCl_3$–MeOH gave pachysandiol-A (0.53 g), needles, mp 291—292°. $[\alpha]_D^{20}$ +14° (c=0.8). Mass Spectrum m/e: 444 (M^+)[5]. *Anal.* Calcd. for $C_{30}H_{52}O_2 \cdot {}^1/_2H_2O$: C, 79.54; H, 12.02. Found: C, 80.05; H, 11.78.

Periodic Acid Oxidation of Pachysandiol-A (I)——To a solution of pachysandiol-A (40 mg) in dioxane (4 ml) was added 30% aqueous solution of $HIO_4 \cdot 2H_2O$ (50 mg) and the mixture was stirred for 4 hr at room temperature. After dilution with water, the mixture was extracted with ether, washed with water, dried ($MgSO_4$), and evaporated. Treatment of the residue with hexane gave a crystalline solid (30 mg). IR ν_{max} cm^{-1}: 2750, 1717 (CHO)[6] NMR τ: 0.15—0.30 (about 2H, CHO)[7]. Attempts for further purification by chromatography and recrystallization resulted in failure, but on addition of EtOH it gave fine needles,[21] mp 185—190°, which showed no longer IR absorption in the carbonyl region.

Partial Acetylation of Pachysandiol-A (I)——A solution of pachysandiol-A (250 mg), acetic anhydride (0.7 ml), and pyridine (0.5 ml) in dry dioxane (3 ml) was allowed to stand overnight at room temperature and the reaction mixture was diluted with water, extracted with CH_2Cl_2. The organic layer was washed successively with 3%HCl and dil. Na_2CO_3, dried ($MgSO_4$), and evaporated. The residue (250 mg) was chromatographed over alumina (5 g) and eluted with benzene (40 ml) to give pachysandiol-A diacetate (IIa) (15 mg), mp 235—236° (CH_2Cl_2–MeOH). Subsequent elution with 1:1 ether–benzene (60 ml) afforded a mixture (200 mg) of isomeric monoacetates (IIb and IIc), which was digested with hexane. The sparingly soluble part was collected by suction and recrystallized from CH_2Cl_2–hexane and then from CH_2Cl_2–MeOH to give 10 mg of pachysandiol-A 3-acetate (IIc), fine needles, mp 290—292°, $[\alpha]_D^{21}$+10° (c=1.16)[22], which was identified with the previously reported pachysandiol-A monoacetate[4] by IR comparison (in KBr). IR ν_{max} cm^{-1}: 3600, 1723, 1250. NMR τ: 5.30 (1H, t, J=about 3 cps, CHOAc), 6.09 (1H, broad, $W^{1/2}$ 7 cps, CHOH), 7.94 (3H, s, Ac), 8.82 (3H, s, *tert*-CH_3), 8.95—9.15 (6 × *tert*-CH_3), 9.20 (3H, d, J=7 cps, *sec*-CH_3). Mass Spectrum m/e: 486 (M^+). *Anal.* Calcd. for $C_{32}H_{54}O_3$: C, 78.96; H, 11.18. Found: C, 78.98; H, 11.19. On the other hand, repeated recyrstallization of the hexane soluble part from CH_2Cl_2–MeOH afforded 150 mg of pachysandiol-A 2-acetate (IIb), needles, mp 245—247°, $[\alpha]_D^{24}$−4° (c=1.0). IR ν_{max} cm^{-1}: 3600, 1723, 1250. NMR τ: 5.05 (1H, q, J=about 3 cps, CHOAc), 6.45 (1H, broad t, J=about 3 cps, CHOH), 7.92 (3H, s, Ac), 8.81 (3H, s, *tert*-CH_3), 8.95—9.15 (7×CH_3). Mass Spectrum m/e: 486 (M^+). *Anal.* Calcd. for $C_{32}H_{54}O_3$:C, 78.96; H, 11.18. Found: C, 78.68; H, 11.31.

Partial Reduction of Pachysandiol-A Diacetate (IIa) with Lithium Aluminum Hydride——To a solution of 200 mg of the diacetate (IIa) in dry ether (20 ml) and dry $CHCl_3$ (10 ml) was added 30 mg of $LiAlH_4$ and the mixture was gently refluxed for 40 min under vigorous stirring. Thereafter, the reaction mixture was treated in the usual manner and the product was chromatographed over alumina (5 g), giving a mixture of isomeric monoacetates (IIb and IIc) (160 mg) and the diol (I), (5 mg). Fractional crystallization of the former as described above afforded 130 mg of 3-acetate (IIc), mp 291—292°, and 8 mg of 2-acetate (IIb), mp 244—247°.

Chromium Trioxide Oxidation of Pachysandiol-A 2-Acetate (IIb)——To a stirred solution of the 2-acetate (IIb) (100 mg) in $CHCl_3$ (15 ml) and AcOH (10 ml) was added gradually a solution of CrO_3 (120 mg) in AcOH–H_2O (100:3, 10 ml) at room temperature and the reaction continued until no starting material could be detected by TLC[23](about 3 hr). After the excess of CrO_3 was decomposed by the addition of MeOH, the reaction mixture was diluted with water and extracted with CH_2Cl_2. The extract was washed with dil. Na_2CO_3, dried ($MgSO_4$), and evaporated. Repeated recrystallizations of the residue (100 mg) from CH_2Cl_2–MeOH gave 2α-acetoxyfriedel-3-one (IVa) as needles (70 mg), mp 260—262°, $[\alpha]_D^{21}$−31° (c=1.0). IR ν_{max} cm^{-1}: 1738, 1723, 1230. NMR τ: 5.05 (1H, t, J=2.5 cps, CHOAc), 7.33 (1H, q, J=7 cps, C_4-H), 7.88 (3H, s, Ac), 8.82 (3H, s, *tert*-CH_3), 8.92—9.30 (7×CH_3). Mass Spectrum m/e: 484 (M^+). *Anal.* Calcd. for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81. Found: C, 79.54; H, 11.06. This compound showed no melting point depression on admixture with the acetate sample, mp 259—262°, derived from authentic cerin and also their IR spectra (KBr) are superimposable.

Chromium Trioxide Oxidation of Pachysandiol-A 3-Acetate (IIc)——The 3-acetate (IIc, 100 mg) was treated with CrO_3 in the same manner as above. The crude product (100 mg) was recrystallized from CH_2Cl_2–MeOH to give 3β-acetoxyfriedel-2-one (Va, 80 mg), mp 255—257°, $[\alpha]_D^{24}$+44° (c=1.0). IR ν_{max} cm^{-1}: 1740, 1230 (OAc), 1723 (C=O). NMR τ: 5.00 (1H, d, J=4 cps, CHOAc), 7.90 (3H, s, Ac), 8.82 (3H, s, *tert*-CH_3), 8.95—9.15 (7×CH_3). Mass Spectrum m/e: 484 (M^+). Anal. Calcd. for $C_{32}H_{52}O_3 \cdot H_2O$: C, 76.44; H, 10.83. Found: C, 76.41; H, 10.57.

Epimerization of 2α-Acetoxyfriedel-3-one (IVa)——The compound IVa (25 mg) was adsorbed onto alumina[15] (5.5 g: 0.8×12 cm column) in benzene and allowed to stand overnight. Thereafter the substance was eluted with benzene–$CHCl_3$ and recrystallized from CH_2Cl_2–MeOH to afford needles (IVb, 20 mg), mp 226—228°, $[\alpha]_D^{20}$−55° (c=1.0). IR ν_{max} cm^{-1}: 1738, 1240 (OAc), 1723 (C=O). NMR τ: 4.81 (1H, q, J=6,

21) This substance is presumably an acetal, but further investigation on its structure could not be achieved.
22) In the preliminary communication (ref. 2) the $[\alpha]_D$ value of pachysandiol-A 3-acetate (IIc) was recorded to be −10° by error.
23) Thin Layer Chromatography, using Merck Kieselgel G acc. to Stahl. Coloring reagent: $Ce(SO_4)_2$ in 10% H_2SO_4.

11 cps, CHOAc), 7.84 (3H, s, Ac), 8.82 (3H, s, *tert*-CH_3), 8.95—9.15 (6×CH_3), 9.27 (3H, s, *tert*-CH_3). Mass Spectrum *m/e*: 484 (M^+). *Anal.* Calcd. for $C_{32}H_{52}O_3$: C, 79.28; H, 10.81. Found: C, 78.95; H, 11.06

Epimerization of 3β-Acetoxyfriedel-2-one (Va)——The compound Va (20 mg) was chromatographed over alumina[15] (5.5 g, 0.8 × 12 cm) and eluted with benzene (60 ml) and with $CHCl_3$ (30 ml). Recrystallizations of the eluate (18 mg), which showed single spot on TLC, from CH_2Cl_2–MeOH gave the epimer (Vb, 15 mg), mp 270—272°, $[\alpha]_D^{22}$ −55° (c=1.0). IR ν_{max} cm^{-1}: 1740, 1235 (OAc), 1723 (C=O). NMR τ: 5.05 (1H, d, J=12 cps, CHOAc), 7.83 (3H, s, Ac), 8.82 (3H, s, *tert*-CH_3), 8.90—9.15 (7× CH_3). Mass Spectrum *m/e*: 484 (M^+) ($C_{32}H_{52}O_3$).

Reduction of 2α-Acetoxyfriedel-3-one (IVa) and Its Epimer (IVb) with Zinc in Acetic Acid——a) To a gently refluxing solution of IVa (20 mg) in AcOH(10 ml) was added zinc powder (2 g) in small portions under vigorous stirring and the reaction continued until the starting material could no longer be detected by TLC (about 2 hr). After dilution with water, the substance was taken in CH_2Cl_2 and the organic layer was washed with dil. Na_2CO_3, dried (K_2CO_3), and evaporated. The residue (15 mg, single spot on TLC) was chromatographed over alumina (3g) from benzene and then recrystallized from CH_2Cl_2–MeOH to give needles (VI) (8 mg), mp 259—260°, $[\alpha]_D^{20}$ −20° (c=1.0). IR ν_{max} cm^{-1}: 1700 (C=O). *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found: C, 83.96; H, 11.72. This compound was identified with friedelin (VI) by mixed melting point determination and IR (KBr) comparison.

b) 2β-Acetoxyfriedel-3-one (IVb, 20 mg) was treated in the same manner as above with zinc powder for 5 hr. The usual working up gave a residue (15 mg) which showed two spots on TLC. This was chromatographed over alumina (3 g) and eluted first with benzene (40 ml) to give friedelin (VI, 8 mg), mp 258—260°, identified by IR (KBr) comparison. Subsequent elution with $CHCl_3$ (40 ml) afforded a crystalline substance (4 mg) whose IR spectrum was identical with that of the starting material (IVb).

Reduction of 3β-Acetoxyfriedel-2-one (Va) and Its Epimer (Vb) with Zinc in Acetic Acid——a) The compound Va (20 mg) was reduced with zinc powder (2 g) in boiling AcOH in the same manner as above. After 40 min, the spot owing to the starting material disappeared on TLC. The product thereby obtained was chromatographed over alumina (3.5 g) in benzene and the eluate (15 mg) was recrystallized from CH_2Cl_2–MeOH to afford friedel-2-one (VIII) as needles (12 mg), mp 287—288°, $[\alpha]_D^{23}$ −7° (c=0.83). IR ν_{max} cm^{-1}: 1700 (C=O). Mass Spectrum *m/e*: 426 (M^+, $C_{30}H_{50}O$).

b) Reduction of the epimer Vb (20 mg) with zinc powder was conducted for 5 hr in the same way as above and the crude product (17 mg: two spots on TLC) was chromatographed over alumina (3.5 g). Elution with benzene gave a single product (10 mg), which on recrystallization afforded friedel-2-one (VIII), mp 286—288° (7 mg). The more polar fraction (5 mg) eluted with $CHCl_3$ was regarded as the starting material (Vb) by IR comparison.

3-Hydroxyfriedel-3-en-2-one (VII)——a) From 2α-Acetoxyfriedel-3-one (IVa): The compound IVa (13 mg) was refluxed with 5% KOH–MeOH (3 ml) for 30 min and then diluted with water, extracted with $CHCl_3$, dried (K_2CO_3), and evaporated to leave a crystalline residue (10 mg) which showed two spots on TLC (approximately 4:1; probably a mixture of the keto-alcohol and VII). This was dissolved in AcOH (2 ml), bismuth trioxide (30 mg) was added, and heated for 30 min in a water bath. After dilution with water, the product was isolated with $CHCl_3$. Recrystallizations of the product (5 mg) with $CHCl_3$–MeOH gave the diosphenol (VII) as needles (3 mg), mp 270—273°, $[\alpha]_D^{20}$ +29° (c=1.0). IR ν_{max} cm^{-1}: 3460, 1668, 1640. UV $\lambda_{max}^{Dioxane}$ mμ (ε): 275 (9650). NMR τ: 4.00 (1H, br, s, OH), 7.2—7.9 (2H, C_1–H_2), 8.18 (3H, s, C_4CH_3), 8.80 (3H, s, *tert*-CH_3), 8.88—9.05 (6 × CH_3). Mass Spectrum *m/e*: 440 (M^+, $C_{30}H_{48}O_2$). *Anal.* Calcd. for $C_{30}H_{48}O_2 \cdot 1^1/_2H_2O$: C, 77.04; H, 11.00. Found: C, 77.53; H, 10.93. This compound was identified with an authentic sample of 3-hydroxyfriedel-3-en-2-one (VII) by IR (KBr) comparison and mixed melting point determination.

b) From 2β-Acetoxyfriedel-3-one (IVb): The compound IVb (20 mg) was treated with 5% KOH–MeOH (5 ml) and then oxidized with bismuth trioxide (20 mg) in the same manner as above. Recrystallization of the product (10 mg) gave 3-hydroxyfriedel-3-en-2-one (7 mg), mp 263—268°, identified by IR (KBr) comparison.

c) From 3β-Acetoxyfriedel-2-one (Va): A solution of 3β-acetoxyfriedel-2-one (Va, 10 mg) in 5% KOH–MeOH (6 ml) was refluxed for 2 hr. Usual working up yielded a crude product (10 mg) which exhibited a single spot on TLC. This was recrystallized from acetone to give the compound VII (6 mg), mp 265—268°, identified by IR (KBr) comparison.

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