Structures of Six Verrucosanes, Novel Carbon Skeletal Diterpenoids from the Liverwort, *Mylia verrucosa* Lindb.

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Six new diterpenoids containing a novel fused 3,6,6,5-tetracyclic ring system, verrucosane, were isolated from the liverwort *Mylia verrucosa* Lindb., and the structures and absolute configurations were determined as (−)-2β,9α-dihydroxyverrucosane (1), (−)-9α-acetoxy-2β-hydroxyverrucosane (2), (−)-2β-hydroxy-9-oxoverrucosane (3), (−)-2β-acetoxy-11α-hydroxyverrucosane (17), (−)-11α-acetoxy-2β-hydroxyverrucosane (24), and (−)-2β-hydroxyverrucosane (26) on the basis of chemical and spectral evidence.

INVESTIGATIONS of terpenic constituents of the liverworts (Hepaticae), which form a unique group in the plant kingdom, have been numerous in recent years. In this laboratory we continue a structural and chemotaxonomical investigation of Japanese liverworts.[1] The present work was undertaken on an ethanol extract of *Mylia verrucosa* Lindb., which grows on rocks and old trees on high land. Six diterpenoids with a new carbon skeleton (named verrucosane) were isolated and their structures determined; part of this work has been reported previously.[2,3] The present paper deals with the chemical and spectral evidence for the proposed structures in detail.

RESULTS AND DISCUSSION

The Structures of (—)-2β,9α-*Dihydroxyverrucosane* (1), 9α-*Acetoxy*-2β-*hydroxyverrucosane* (2), and 2β-*Hydroxy*-9-*oxoverrucosane* (3).—(—)-2β,9α-Dihydroxyverrucosane was isolated as a major component of the ethanol extract as colourless crystals, m.p. 153—154 °C. It analysed for $C_{20}H_{34}O_2$, and was characterized as a diterpene alcohol containing two secondary hydroxy groups [$\nu_{max.}$ 3 525 and 3 400 cm^{-1}; δ 3.45—3.80 (2 H, complex m)], a cyclopropane ring [$\nu_{max.}$ 3 060, 1 012, and 1 005 cm^{-1}; δ 0.1—0.7 (3 H, m)], an isopropyl group [$\nu_{max.}$ 1 385 and 1 375 cm^{-1}; δ 0.83 and 0.90 (each 3 H, d, *J* 7 Hz)], and three tertiary methyls [δ 0.77, 1.03, and 1.20 (each 3 H, s)].

(—)-9α-Acetoxy-2β-hydroxyverrucosane was isolated as a viscous oil, $C_{22}H_{36}O_3$, containing a secondary acetoxy-group [$\nu_{max.}$ 1 735 and 1 252 cm^{-1}; δ 2.00 (3 H, s, OAc), and 4.14 (1 H, t, *J* 2.5 Hz, CH_2CHOAc)] and a secondary hydroxy-group [δ 3.54 (1 H, d, *J* 10 Hz, CHOH)], together with the cyclopropane ring, isopropyl group, and three tertiary methyls which were present in the first compound.

(—)-2β-Hydroxy-9-oxoverrucosane was isolated as colourless prisms, $C_{20}H_{32}O_2$, m.p. 110—111.5 °C; it contained a carbonyl group [ν 1 695 cm^{-1}; δ 1.87 and 2.47 (each 1 H, d, *J* 15 Hz, CH_2CO)] and a secondary hydroxy-group [δ 3.67 (1 H, d, *J* 8.5 Hz, CHOH)], together with a cyclopropane ring, an isopropyl group, and three tertiary methyls.

Acetylation of the diol (1) with acetic anhydride in pyridine gave a monoacetate, $C_{22}H_{36}O_3$, which was identical with the naturally occurring acetoxyalcohol (2) on the basis of spectral and physical properties. The original diol exhibited a complex signal due to two secondary carbinyl protons in the region between δ 3.45 and 3.80 of the ^1H n.m.r. spectrum, while the monoacetate showed a doublet (1 H, *J* 10 Hz) due to the secondary carbinyl proton at δ 3.55 and a triplet (1 H, *J* 2.5 Hz) due to the acetoxy-bearing methine at δ 4.74. Based on these facts, it is certain that the diol was a tetracyclic diterpenoid containing two secondary hydroxy-groups.

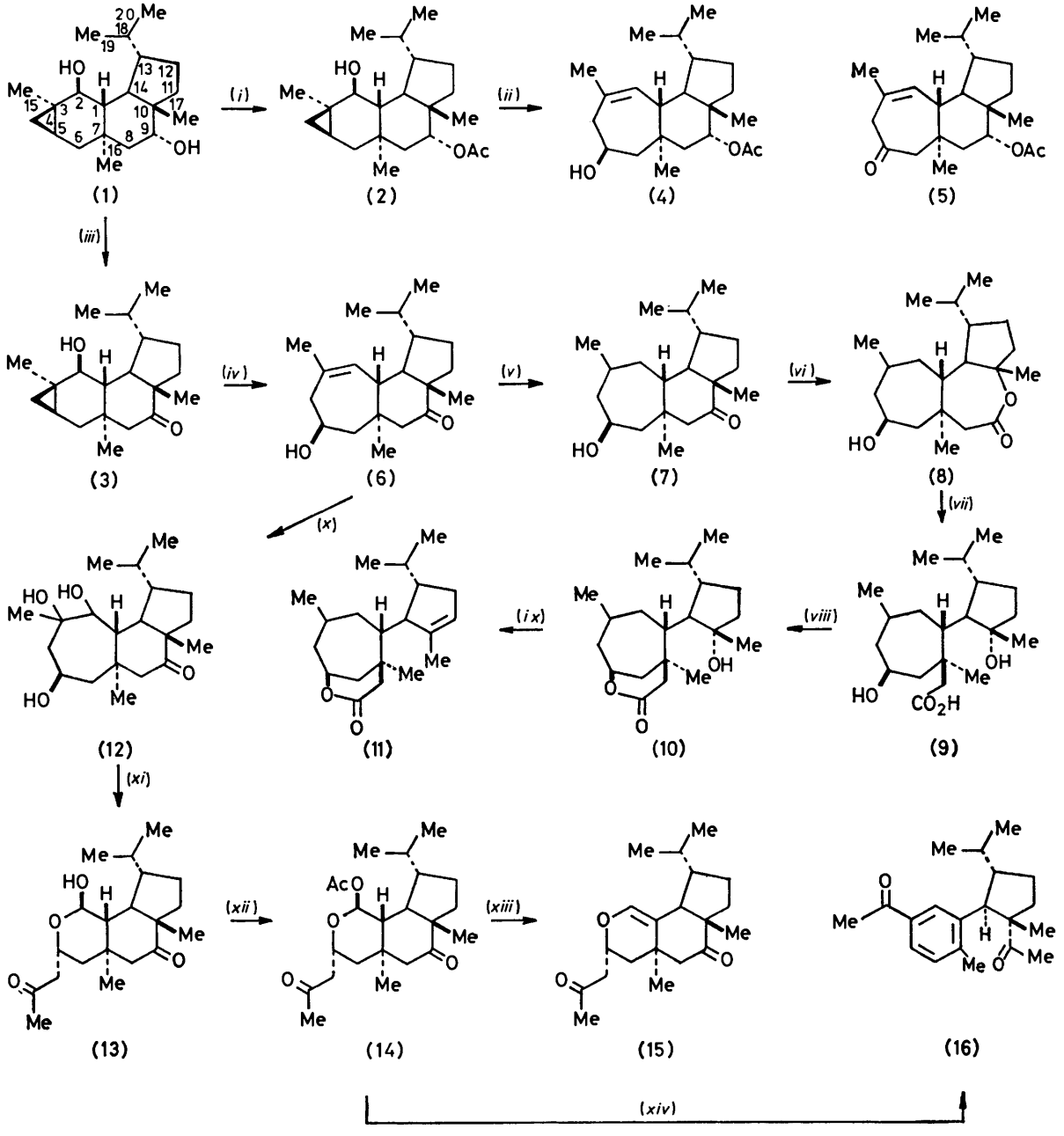
Oxidation of the diol with Jones reagent afforded a hydroxy-ketone, $C_{20}H_{32}O_2$, which was identical with the naturally occurring hydroxyketone (3). The i.r. absorption band ($\nu_{max.}$ 1 695 cm^{-1}) due to the carbonyl group suggested the hydroxy-ketone to be part of a six-membered (or larger) ring. In the ^1H n.m.r. spectrum there was an AB quartet due to an active methylene adjacent to the carbonyl group at δ 1.87 and 2.47 (*J* 15 Hz) together with the doublet (δ 3.67) of the secondary carbinyl proton, which corresponded to that of the monoacetate (2). Accordingly, the two hydroxy-groups in the original diol should be present as partial structures of $C{-}CH_2{-}CH(OH){-}C$ and $C{-}CH(OH){-}CH$.

When refluxed with 0.5N-H_2SO_4–acetone (1 : 4), the monoacetate (2) and the hydroxy-ketone (3) were respectively converted to a homoallyl acetoxy-alcohol (4), $C_{22}H_{36}O_3$, and a homoallyl keto-alcohol (6), $C_{20}H_{32}O_2$, in good yields. In both derivatives the cyclopropane ring and the hydroxy-group which were originally present disappeared, and another secondary hydroxy-group and a trisubstituted double bond bearing a methyl group were formed. Such structural isomerization on acid treatment could be reasonably explained in terms of homoallylic ring expansion of a cyclopropyl methanol moiety as shown by Gasic *et al.*[4]

The acetoxy-alcohol (4) was then oxidized with Jones reagent at room temperature to give the acetoxy-ketone (5), $C_{22}H_{34}O_3$, whose ^1H n.m.r. spectrum showed two AB quartets attributable to the two methylene groups attached to the carbonyl, at δ 2.20 and 2.43 (each 1 H, d, *J* 12 Hz) and at δ 2.62 and 3.50 (each 1 H, d, *J* 17 Hz). Irradiation at δ 3.50 caused the doublet at δ 2.62 to collapse to a singlet, and irradiation at δ 5.61 (olefin proton) re-formed the broad doublet at δ 3.50 into a sharp doublet (*J* 17 Hz), showing the presence of a small allylic coupling. Such spectral behaviour showed (5) to have the partial structure $C{-}CH_2{-}CO{-}CH_2{-}CMe{=}CH{-}CH$, which must comprise a seven-membered ring as shown by the series of the degradations described below.

In the ^1H n.m.r. spectrum of the diol (1), the C-1 proton was detected at δ 0.9 by irradiation of the secondary carbinyl proton (δ 3.50, 1 H, d, *J* 10 Hz), but the proton was at much higher field than an ordinary methine proton. This fact could be explained by the anisotropic effect of the cyclopropane ring.[5] Hence, the cyclopropane ring and the C-1 proton should be placed on the same side of ring A. It has been reported that a cyclopropylmethanol containing a secondary hydroxy-group and a cyclopropane ring in the *cis* configuration underwent facile ring expansion to give a homoallylic secondary alcohol which had the newly formed secondary hydroxy-group *cis* to the cyclopropane ring.[4] Thus, this part of the diol should be represented by the stereostructure (A).

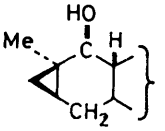
The homoallyl keto-alcohol (6), *via* catalytic hydrogenation, Baeyer–Villiger reaction, and treatment with 5% methanolic potassium hydroxide, in turn, was converted to a dihydroxy-acid (9), $C_{20}H_{36}O_4$, which on treatment with acetic anhydride furnished a six-membered lactone (10), $C_{20}H_{34}O_3$, in good yield. Such easy formation of the lactone indicated that ring B was six-membered in the diol, and that the C-5 hydroxy-group and the C-7 carboxymethyl group were on the same side of ring A and



SCHEME 1 (*i*), Ac_2O–pyridine; (*ii*), 0.5N–H_2SO_4; (*iii*) Jones reagent; (*iv*), 0.5N–H_2SO_4; (*v*), PtO_2; (*vi*), *m*-chloroperbenzoic acid; (*vii*), KOH; (*viii*), Ac_2O, heat; (*ix*), $SOCl_2$–pyridine; (*x*), OsO_4; (*xi*), $NaIO_4$; (*xii*), Ac_2O–pyridine; (*xiii*), heat; (*xiv*), NaOH

methyl ethyl group at C-7 was *trans* to the hydroxy-group in compound (9). Hence, the A and B ring junction should be *trans* in all the compounds, because the C-1 proton was *cis* to the hydroxy-group at C-5 or C-2. Further treatment of (10) with $SOCl_2$ in pyridine at room temperature gave exclusively a cyclopentene derivative (11), $C_{20}H_{32}O_2$, containing a trisubstituted double bond bearing a methyl group. This fact indicated that the B and C ring junction was also *trans*, because the dehydration is known to occur *via trans* elimination.

Based on the molecular formula the remaining part (ring C) of the verrucosane skeleton should be a cyclopentane ring bearing an isopropyl group, whose presence was indicated by the absorption band at *ca.* 1 170 cm^{-1}, the split band near 1 380 cm^{-1},[6] and two doublets (J 7 Hz) of methyl signals at δ *ca.* 0.8 in the i.r. and ^1H n.m.r.



(A)

spectra of all derivatives. The 2,3,5-triol (12), $C_{20}H_{34}O_4$, which was prepared by oxidation of the homoallylic alcohol (6) with OsO_4, was subjected to glycol fission to give directly the hemiacetal (13), $C_{20}H_{32}O_4$, whose acetate (14), $C_{22}H_{34}O_5$, gave a vinyl ether (15), $C_{20}H_{30}O_2$, on pyrolysis and a 3,4-disubstituted acetophenone (16), $C_{20}H_{28}O_2$, on treatment with 5% methanolic sodium hydroxide, both in good yield. In the ^1H n.m.r. spectra the last compound showed a signal due to the benzyl methine group at δ 3.83 (J 8 Hz). This coupling constant indicated that the cyclopentane ring was present in the envelope conformer, with the C-13 and C-14 hydrogens being *trans*-diaxial. Thus, the 3,4-disubstituted acetophenone should be represented by stereostructure (16), which was also supported by the off-resonance ^{13}C n.m.r. spectrum, which consisted of six singlets, six doublets, two triplets, and six quartets.

The formation of the acetophenone derivative (16) from the acetylated hemiacetal (14) is reasonably explained by successive hydrolysis, aldol condensation, dehydration, and retro-Michael type reaction.

On the basis of the above chemical and spectral evidence, the structure of the diol was determined to be the stereostructure which contained a novel fused 3,6,6,5-tetracyclic ring system in the *cis-trans-anti-trans*-configuration (1). Since the carbon skeleton was named verrucosane, the diol is (−)-2β,9α-dihydroxyverrucosane. That the absolute configuration of this compound is as in (1) is also based on the negative Cotton effect in the o.r.d. spectra of the ketone (3), $[\phi_{min.}]_{316}$ −5 780, $[\phi_{max.}]_{274}$ +1 390, and the ketone (6), $[\phi_{min.}]_{316}$ −2 530, $[\phi_{max.}]_{270}$ +1 170.*

The structures and absolute configurations of the monoacetate (2) and the hydroxyketone (3) which were isolated from the same liverwort, were thus also determined along with that of the diol (1).

The Structure of (−)-2β-*Acetoxy*-11α-*hydroxyverrucosane* (17).—The fourth compound, $C_{22}H_{36}O_3$, was isolated as colourless needles, m.p. 203—204 °C. Although, like compound (2), compound (17) contained a secondary acetoxy [$\nu_{max.}$ 1 707 and 1 260 cm^{-1}; δ 4.93 (1 H, d, J 9 Hz)], a secondary hydroxy [$\nu_{max.}$ 3 495 cm^{-1}; δ 3.95 (1 H, d, J 5 Hz)] and the common functional groups of the verrucosane skeleton, the compounds differed in their spectra. During prolonged storage at room temperature, compound (17) underwent spontaneous hydrolysis to give the diol (18), $C_{20}H_{34}O_2$, as colourless prisms, m.p. 132—133 °C; in the ^1H n.m.r. spectrum of this diol, one secondary carbinyl proton (δ 3.68, d, J 9 Hz) showed the same pattern and coupling constant as the secondary C-2 carbinyl proton of the diol (1). In addition, acid treatment of the diol (18) afforded a homoallylic alcohol (19), $C_{20}H_{34}O_2$. These facts indicated that (17) was a 2-acetoxyverrucosane, with the hydroxy in a position other than at C-9.

To determine the position of the hydroxy, the compound was subjected to Jones oxidation, which converted it to a cyclic five-membered ketone (20), $C_{22}H_{34}O_3$. However, the i.r. spectrum of the product showed the ester and ketone bands were overlapping at 1 735 cm^{-1}. When the ketone was heated with 0.5N-H_2SO_4–acetone, it underwent hydrolysis of the acetoxy and homoallylic ring expansion of the cyclopropyl methanol moiety to give the cyclic five-membered ketone (22), $C_{20}H_{32}O_2$, ($\nu_{max.}$ 1 735 cm^{-1}), which had a trisubstituted double bond bearing a methyl group and a secondary hydroxy. The formation of this cyclic five-membered ketone revealed that compound (17) had the hydroxy on ring C. In the ^1H n.m.r. spectrum of the acetoxyketone (20), the methylene adjacent to the carbonyl group (δ 2.20—2.90) and the methyl group on C-10 (δ 1.01), both showed remarkable down-field shifts to δ 3.83 and 4.37, and δ 2.05, respectively, on addition of $Eu(fod)_3$ (0.3 mol. equiv.), the former appearing as a pair of double doublets. This spectral result assigned the hydroxy to C-11.

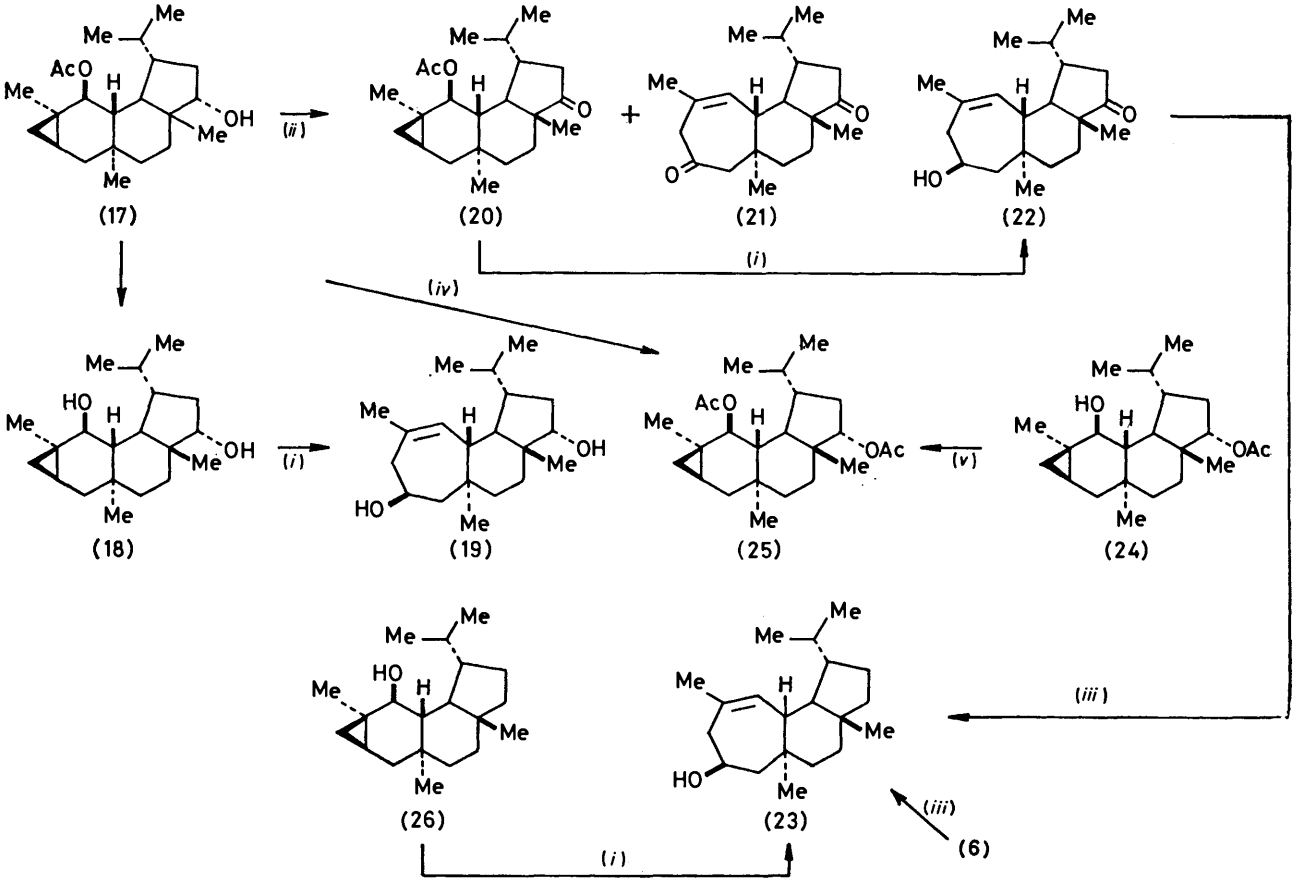
The C-11 hydroxy is probably *trans* to the C-10 methyl, because ^1H n.m.r. spectra of (18) and (19) showed a small solvent shift [$\Delta\delta(CDCl_3 - C_5D_5N)$ −0.10 and −0.06 p.p.m. for (18) and (19) respectively] for the C-10 methyl group.† Further confirmation of the verrucosane skeleton of the compound was achieved by reduction of the keto-alcohol (22) into a homoallylic alcohol (23), $C_{20}H_{34}O$, *via* the tosylhydrazone, which was identical with the homoallylic alcohol obtained in similar treatment of the keto-alcohol (6). Thus, the structure and absolute configuration of the compound may be represented by the stereostructural formula (17).

The Structure of (−)-11α-*Acetoxy*-2β-*hydroxyverruco-*

* Compound (3): c 0.350 in dioxan; (6): c 0.390 in dioxan.

† The solvent shifts and tabulated ^1H n.m.r. data are in Supplementary Publication No. SUP 22554 (3 pp.). For details of the Supplementary Publication scheme see *J.C.S. Perkin I*, 1978, Index issue.

sane (24).—The fifth compound, $C_{22}H_{36}O_3$, m.p. 203—204 °C, was the same as compound (17) in terms of the molecular formula and functional groups. However, the secondary carbinyl proton and the methine group bearing the acetoxy had ^1H n.m.r. splitting patterns and coupling constants which were compared to compound (17). This suggested that the positions of the hydroxy and acetoxy groups were exchanged between compounds



SCHEME 2 (*i*), 0.5N–H_2SO_4; (*ii*), Jones reagent; (*iii*) $TSNHNH_2$, $NaBH_4$; (*iv*), AcCl–pyridine; (*v*) Ac_2O–pyridine, heat

(17) and (24). Compound (24) was acetylated with acetic anhydride in pyridine to afford a diacetate, $C_{24}H_{38}O_4$, which was identical with the diacetate (25) prepared by similar treatment of the alcohol (17). Accordingly, the compound was unambiguously determined to be (—)-11α-acetoxy-2β-hydroxyverrucosane.

The Structure of (—)-2β-*Hydroxyverrucosane* (26).—The sixth compound, $C_{20}H_{34}O$, m.p. 76.5—78 °C, was the least polar. It contained a secondary hydroxy together with all the functional groups of the verrucosane skeleton. On treatment with 0.5N-H_2SO_4–acetone solution, the compound underwent the homoallylic expansion of the cyclopropyl methanol moiety to give a secondary alcohol which was identical with the alcohol (23), derived from the keto-alcohol (6) and (22). Thus, the compound was determined to be (—)-2β-hydroxyverrucosane.

EXPERIMENTAL

The spectra were taken on a JASCO ORD UV-5 (o.r.d.), Shimadzu IR-400 (i.r.), JEOL JNM-4H-100 and HL-60C (n.m.r.), Hitachi ESP-3T (u.v.), JEOL JMS-OISG-2 (mass spectrometry) spectrometers. The optical rotations were measured in $CHCl_3$ solutions on a Yanaco OR-50 and the elemental analyses were carried out on a Yanagimoto CHN Corder MT-2.

Extraction and Isolation.—The liverwort was collected at Akaishi-san in Shikoku, Japan, and dried in the shade. The dried matter (4.8 kg), after being extracted with hexane (18 l), was digested with ethanol (18 l) at room temperature for 3 d (3 ×). The ethanol solutions were combined and evaporated *in vacuo* to give a viscous oil. This was dissolved in ether (500 ml), washed with 3% aqueous NaOH solution, 3% HCl, and a saturated aqueous solution of NaCl, dried over anhydrous Na_2SO_4, and the solvent evaporated off to give a neutral dark green viscous oil (75 g). This was then chromatographed over a column of silica gel [1 kg, 0.063 mm (Merck)] using the following mixed solvents stepwise. Fractions 1 and 2: hexane–ethyl acetate (v/v 100 : 2); fractions 3—5: hexane–ethyl acetate (100 : 5); fractions 6—8: hexane–ethyl acetate (100 : 10); fractions 9—11: hexane–ethyl acetate (100 : 15); fractions 12 and 13: hexane–ethyl acetate (100 : 30); and fractions 14 and 15: hexane–ethyl acetate (2 : 1). Each fraction was of volume 300 ml.

Isolation of (—)-2β,9α-*Dihydroxyverrucosane* (1).—Eva-

poration of the solvent from fraction 8 gave a crystalline substance (1.5 g) showing one spot (R_F 0.5) on t.l.c. using silica gel and benzene–hexane–ethanol (10 : 10 : 1), which was recrystallized from hexane–ethyl acetate (20 : 1), m.p. 153—154 °C; $[\alpha]_D$ −72° (c 1.18); $\nu_{max.}$ (KBr) 3 525, 3 400, 3 060, 1 385, 1 375, 1 170, 1 030, and 1 012 cm^{-1}; *m/e* 306 (M^+, 17%), 288 (M^+ − 18, 88), 270 (62), 255 (40), 227 (59), 189 (44), 147 (35), 123 (40), 107 (42), 97 (42), 81 (42), 69 (44), 43 (98), and 41 (100); $\delta_C(CDCl_3)$ 23.4, 36.8, and 48.5 (each s), 25.2, 29.1, 40.3, 43.0, 46.3, 73.4, and 73.5 (each d), 18.3, 21.8, 32.9, 42.3, and 43.9 (each t), and 15.1, 19.1, 21.2, 22.2, and 23.4 (each q) (Found: C, 78.45; H, 11.30. Calc. for $C_{20}H_{34}O_2$: C, 78.38; H, 11.18%).

Isolation of (−)-9α-*Acetoxy*-2β-*hydroxyverrucosane* (2).—Fractions 6 and 7 contained respectively another component (R_F 0.50) which partially overlapped the diol (1) (R_F 0.43) on t.l.c. [benzene–hexane–ethyl acetate (15 : 8 : 3)]. These fractions were combined, concentrated, and developed by preparative t.l.c. [benzene–hexane–ethanol (10 : 10 : 1)] to separate (−)-9α-acetoxy-2β-hydroxyverrucosane (1.2 g) as a viscous substance; $[\alpha]_D$ −82.7° (*c* 1.2); $\nu_{max.}$ (CCl_4) 3 600, 3 525, 3 060, 1 735, 1 390, 1 380, 1 250, and 1 035 cm^{-1}; *m/e* 348 (M^+, 1%), 330 (M^+ − 18, 7), 306 (M^+ − 42, 3), 270 (30), 255 (10), 227 (10), 202 (7), 201 (7), 147 (11), 119 (19), 107 (18), 105 (13), 95 (20), 93 (17), 91 (12), 81 (25), 69 (26), 55 (37), 43 (100), and 41 (67) (Found: C, 75.75; H, 10.20. Calc. for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41%).

Isolation of (−)-2β-*Hydroxy*-9-*oxoverrucosane* (3).—Evaporation of the solvent from fraction 9 gave a semi-crystalline substance showing one spot on t.l.c., which was recrystallized from hexane–ethyl acetate (20 : 1) to give the keto-alcohol (1 g) as colourless prisms, m.p. 110—111.5 °C; $[\alpha]_D$ −103.2° (*c* 0.9); $\nu_{max.}$ (KBr) 3 540, 3 075, 2 920, 2 875, 1 695, 1 410, and 1 038 cm^{-1}; *m/e* 304 (M^+, 3%), 280 (M^+ − 18, 41), 119 (100), 117 (66), 109 (44), 108 (46), 81 (48), 55 (48), 43 (54), and 41 (96) (Found: C, 77.95; H, 11.15. Calc. for $C_{20}H_{32}O_2$: C, 78.03; H, 11.03%).

Acetylation of the Diol (1).—The diol (100 mg) was dissolved in pyridine (3 ml) and acetic anhydride (1 ml) added. After being set aside overnight at room temperature, the mixture was worked up in the usual way to give a crude monoacetate (50 mg), which was purified by means of preparative t.l.c. [benzene–hexane–ethanol (10 : 10 : 1)]; $[\alpha]_D$ −76° (*c* 0.5). The monoacetate thus obtained was identical (i.r. and n.m.r. spectra) wtih the (−)-9α-acetoxy-2β-hydroxyverrucosane (2) isolated from the same plant.

Oxidation of the Diol (1).—The diol (330 mg) was mixed with an excess of Jones reagent (5 ml) in acetone (10 ml) and the mixture was stored at 0 °C for 5 min. The reacted mixture was then poured into water and the aqueous solution was extracted with ether. The ethereal solution was dried over anhydrous Na_2SO_4, and the solvent was evaporated off to afford a crude crystalline substance (300 mg), which was recrystallized from hexane–ethyl acetate (20 : 1) to give colourless prisms, m.p. 110—112 °C, $[\alpha]_D$ −130° (*c* 1.1). The oxidation product was identical with the naturally-occurring (−)-2β-hydroxy-9-oxoverrucosane (3) (i.r. and n.m.r. spectra), and showed no depression in a mixed m.p. determination

Acid Treatment of the Acetoxy-alcohol (2).—The acetoxy-alcohol (40 mg) was dissolved in acetone (8 ml)–0.5N-H_2SO_4 (2 ml), and the solution was heated under reflux for 2 h. The reacted mixture was diluted with water and extracted with ether. The residue obtained after the evaporation of the ether was purified by preparative t.l.c. with benzene–hexane–ethanol (10 : 10 : 1) to give a homoallyl acetoxy-alcohol (4) (38 mg) as a viscous liquid; $[\alpha]_D$ −14.1° (*c* 1.8); $\nu_{max.}$ (CCl_4) 3 355, 1 720, 1 240, and 1 020 cm^{-1}. δ 0.83, 0.87, 0.89, and 0.93 (each 3 H, s, Me-C and Me_2CH), 1.78 (3 H, s, =C–Me), 2.03 (3 H, s, OCOMe), 3.62 (1 H, br t, *J* 10 Hz, HO–C–H), 4.83 (1 H, t, *J* 2.5 Hz, AcO–C*H*), and 5.37 (1 H, br d, *J* 5 Hz, =C–H); *m/e* 348 (M^+, 3%), 330 (14), 289 (26), 270 (38), 228 (41), 119 (52), 108 (33), 81 (36), 69 (38), 55 (37), and 43 (100).

Oxidation of the Homoallyl Acetoxy-alcohol (4).—The acetoxy-alcohol (35 mg) was oxidized with an excess of Jones reagent in acetone (3 ml) at 0 °C. The reacted mixture was treated according to the usual procedure and purified by preparative t.l.c. [benzene–hexane–ethanol (10 : 10 : 1)] to give an acetoxy-ketone (5) (29 mg) as colourless needles, m.p. 110—111 °C; $[\alpha]_D$ −97.7° (*c* 2.1); $\nu_{max.}$ (KBr) 1 730, 1 700, 1 430, 1 240, 1 020, and 1 010 cm^{-1}; δ 0.88 and 1.04 (each 3 H, s, Me–C), 0.86 and 0.92 (each 3 H, s, Me_2CH), 1.82 (3 H, s, =C–Me), 2.05 (3 H, s, OCOMe), 2.20 and 2.44 (each 1 H, d, *J* 12 Hz, $COCH_2$), 2.26 and 3.50 (each 1 H, d, *J* 17 Hz, =C–CH_2–CO), 4.87 (1 H, t, *J* 3 Hz, AcO–C*H*), and 5.61 (1 H, br d, *J* 7 Hz, =C–H). The above assignment of the n.m.r. signals was established by spin-decoupling experiments. Irradiation at δ 2.20 collapsed the doublet at δ 2.44 to a singlet, and irradiation at δ 3.50 transformed the sharp doublet at δ 2.62 to a sharp singlet, and simplified the broad doublet at δ 5.61 to a sharp doublet; conversely, irradiation at δ 5.61 simplified the signal at δ 3.50. *m/e* 346 (M^+, 12%), 304 (6), 243 (16), 190 (42), 186 (27), 119 (54), 96 (41), 93 (38), 91 (33), 81 (38), 69 (33), 55 (56), and 43 (100) (Found: C, 76.15; H, 9.70. Calc. for $C_{22}H_{34}O_3$: C, 76.26; H, 9.89%).

Acid Treatment of the Hydroxy-ketone (3).—The hydroxy-ketone (130 mg) was dissolved in 0.5N-H_2SO_4–acetone (v/v 1 : 4) (10 ml), and heated under reflux for 5 h. The reacted mixture was poured into a large amount of water and taken up into ether. The ethereal solution was washed with 5% $NaHCO_3$ solution and saturated aqueous NaCl, and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave a crude crystalline substance, which was purified by preparative t.l.c. [benzene–hexane–ethanol (10 : 10 : 1)] and recrystallized from hexane–ethyl acetate to afford the homoallyl keto-alcohol (6) (120 mg) as colourless prisms, m.p. 133—135 °C; $[\alpha]_D$ −35.0° (*c* 0.9); $\nu_{max.}$ (KBr) 3 250, 1 715, 1 030, and 877 cm^{-1}; δ 0.84 and 0.90 (each 3 H, d, *J* 7 Hz, Me_2CH), 0.91 and 1.15 (each 3 H, s, Me–C), 1.81 (3 H, s, =C=Me), 3.62 (1 H, br t, *J* 10 Hz, HO–C–H), and 5.31 (1 H, br d, *J* 7 Hz, =C–H); *m/e* 304 (M^+, 34%), 286 (21), 243 (24), 220 (23), 159 (21), 149 (28), 123 (59), 119 (54), 107 (86), 94 (51), 93 (72), 91 (62), 81 (100), 69 (83), 55 (50), and 41 (90) (Found: C, 78.95; H, 10.65. Calc. for $C_{20}H_{32}O_2$: C, 78.89; H, 10.59%).

Catalytic Hydrogenation of the Homoallyl Keto-alcohol (6).—Catalytic hydrogenation of the compound (150 mg) was carried out over PtO_2 (10 mg) in acetic acid (5 ml) at room temperature. The reacted mixture was poured into water, neutralized with aqueous Na_2CO_3. and extracted with ether. The ethereal extracts were washed with saturated aqueous NaCl, dried over Na_2SO_4, and the solvent evaporated off under reduced pressure. The residue was purified by preparative t.l.c. to give the dihydroketo-alcohol (7) (140 mg) as colourless needles, m.p. 117—118 °C; $\nu_{max.}$ (KBr) 3 280, 1 715, 1 430, and 1 015 cm^{-1}; δ 0.75 and 0.88 (each 3 H, d, *J* 7 Hz, Me_2CH), 0.95 and 1.12 (each 3 H, s, Me–C), 0.97 (3 H, d, *J* 9 Hz, *Me*–CH), and 4.00 (1 H, m, $W_{\frac{1}{2}}$

20 Hz, HO–C–H); *m/e* 306 (M^+, 18%), 288 ($M^+ - 18$, 9), 124 (32), 110 (46), 97 (48), 81 (70), 69 (58), 55 (64), 43 (34), and 41 (100).

Baeyer–Villiger Reaction of the Dihydroketo-alcohol (7).—To a solution of the compound (150 mg) in ethanol-free chloroform (6 ml) was added a chloroform solution (4 ml) of *m*-chloroperbenzoic acid, and the mixture was stirred at room temperature for 30 h. The reacted mixture was then washed with $NaHSO_3$, 5% NaOH, and saturated aqueous NaCl, dried over Na_2SO_4, and the solvent distilled off to afford the lactone as a colourless oily substance, which was purified by preparative t.l.c. [hexane–ethyl acetate (5 : 1)]. The lactone (100 mg) was recrystallized from hexane to give colourless needles, m.p. 122.5—123 °C; $\nu_{max.}$ (KBr) 3 460, 1 704, 1 310, 1 200, 1 100, and 1 025 cm^{-1}; δ 0.89 and 1.00 (each 3 H, d, *J* 7 Hz, Me_2CH), 1.05 (3 H, d, *J* 7.5 Hz, *Me*–CH), 0.93 (3 H, s, Me–C), 1.50 (3 H, s, O–C–Me), 2.43 and 3.03 (each 1 H, d, *J* 16 Hz, CO–CH_2–C), and 4.11 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, HO–C–H); *m/e* 322 (M^-, 3%), 304 ($M^+ - 18$, 6), 196 (45), 179 (100), 164 (28), 123 (74), 110 (86), 81 (50), 69 (52), 55 (62), 43 (91), and 41 (68).

Alkaline Hydrolysis of the Lactone (8).—The lactone (130 mg) was added to a solution of KOH (200 mg) in a mixture of methanol (5 ml) and water (3 ml), and the mixed solution was allowed to stand at 32 °C for 4 h. The reacted mixture was poured into water, acidified with dilute HCl, and taken up into chloroform. The chloroform solution was washed with saturated aqueous NaCl, dried over Na_2SO_4, and the solvent was distilled out. The crude reaction product thus obtained was purified by preparative t.l.c. to give the dihydroxy-acid (9) (105 mg) in a semi-crystalline state; $\nu_{max.}$ (KBr) 2 300—3 700, 3 500, 1 720, 1 210, and 1 020 cm^{-1}; δ(CD_3OD) 0.90 and 1.00 (each 3 H, d, *J* 7 Hz, Me_2CH), 0.95 (3 H, s, Me–C), 1.07 (3 H, d, *J* 7 Hz, *Me*–CH), 1.57 (3 H, s, HO–C–*Me*), 2.22 and 2.50 (each 1 H, d, *J* 12.5 Hz, HO_2C–CH_2–C), and 3.95 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, HO–C–H); *m/e* 322 ($M^+ - 18$, 4), 261 (22), 253 (15), 196 (17), 179 (15), 161 (17), 136 (26), 135 (30), 123 (41), 121 (41), 109 (69), 95 (52), 93 (37), 81 (57), 69 (57), 55 (65), 43 (100), and 41 (65).

Lactonization of the Dihydroxy-acid (9).—The acid (100 mg) was dissolved in acetic anhydride (8 ml) and heated under reflux for 3 h. The reacted mixture was cooled, poured into water, and taken up into ether (80 ml). The ethereal solution was washed with 5% $NaHCO_3$ and saturated aqueous NaCl, dried over Na_2SO_4, and the solvent evaporated. The reaction product thus obtained was purified by preparative t.l.c. to furnish the six-membered lactone (10) as a colourless viscous oil (85 mg); ν(CCl_4) 3 450, 1 720, 1 395, 1 384, 1 245, and 1 130 cm^{-1}; δ 0.8—1.3 (12 H, 4 × Me), 1.57 (3 H, s, HO–C–*Me*),3.00 (1 H, d, *J* 16 Hz, $OCOCH_2$), and 4.83 (1 H, m, $W_{\frac{1}{2}}$ 12 Hz, HO–C–H); *m/e* 322 (M^+, 4%), 304 ($M^+ - 18$, 3), 289 (2), 278 (5), 261 (13), 252 (25), 195 (14), 161 (15), 149 (33), 136 (27), 135 (25), 123 (28), 121 (31), 109 (38), 107 (26), 95 (39), 93 (31), 81 (49), 71 (34), 69 (56), 55 (62), 43 (100), and 41 (76).

Dehydration of the Lactone (10).—Thionyl chloride (0.2 ml) was added to a cooled solution of the lactone (80 mg) in pyridine (2 ml), and the mixture was allowed to react for 1 h at room temperature. The reacted mixture was poured into ice–water and taken up into ether. The ethereal solution was washed with 2N-H_2SO_4 and 2N-Na_2CO_3, dried over Na_2SO_4, and the solvent was evaporated off, leaving an unsaturated lactone (11) (55 mg) which was purified by preparative t.l.c.; $\nu_{max.}$ (CCl_4) 1 720, 1 220, 1 025, and 985 cm^{-1}; δ 0.64 and 0.87 (each 3 H, d, *J* 7 Hz, Me_2CH), 0.96 (3 H, d, *J* 7 Hz, H–C–*Me*), 1.03 (3 H, s, Me–C), 4.83 (1 H, m, $W_{\frac{1}{2}}$ 16 Hz, O–C–H), and 5.37 (1 H, br s, =C–H).

Oxidation of the Homoallyl Keto-alcohol (6).—To a solution of the compound (6) (95 mg) in a mixture of dry benzene–dry pyridine (10 : 1; 5.5 ml) was added a solution of OsO_4 (200 mg) in benzene (2 ml) under cooling in an ice-bath, and the mixture was allowed to react at room temperature for 6 d. The solvent was distilled out, the residual substance was dissolved in ethanol (10 ml), and the solution was mixed with a solution of Na_2SO_3 (1 g) in water (10 ml). The mixed solution was heated under reflux for 2 h, and the resulting precipitates were filtered off and the filtrate was extracted with chloroform. The chloroform solution was washed with saturated aqueous NaCl, dried, and the solvent was evaporated off. The reaction product thus obtained was purified by preparative t.l.c. using a mixed solvent (benzene–chloroform–hexane–ethanol, 2 : 2 : 1 : 1) to give a 2,3,5-triol (12) (70 mg), homogeneous on t.l.c. (benzene–ethyl acetate, 1 : 1) (R_F 0.6), m.p. 127.5—129 °C; $\nu_{max.}$ (KBr) 3 530, 3 380, 1 730, 1 700, 1 425, 1 165, 1 030, and 1 015 cm^{-1}; δ(CD_3OD) 0.78 and 0.94 (each 3 H, d, *J* 6.5 Hz, Me_2CH), 0.92 (3 H, s, Me–C), 1.18 (3 H, s, Me), 1.33 (3 H, s, HO–C–*Me*), and 3.6—4.2 (2 H, m, $W_{\frac{1}{2}}$ 22 Hz); *m/e* 338 (M^+, 5%), 320 ($M^+ - 18$, 24), 262 (11), 238 (24), 220 (24), 122 (48), 109 (40), 95 (57), 81 (67), 55 (65), 43 (100), and 41 (71).

Oxidation of the 2,3,5-*Triol* (12).—To a solution of (12) (70 mg) in methanol (3 ml) was added a solution of $NaIO_4$ (100 mg) in water (4 ml), and the mixture was allowed to react at room temperature for 10 d. The reacted mixture was diluted with water, extracted with ether, and the ethereal solution, after being dried, was evaporated to give the hemiacetal (13) as a viscous substance. It was purified by preparative t.l.c.; $\nu_{max.}$ (CCl_4) 3 600, 3 400, 1 710, 1 035, and 970 cm^{-1}; δ 0.77 and 0.90 (each 3 H, d, *J* 7.5 Hz, (Me_2CH), 1.03 and 1.15 (each 3 H, s, Me–C), 2.20 (3 H, s, COMe), 4.60 (1 H, m, $W_{\frac{1}{2}}$ 28 Hz, O–C–H), and 5.01 (1 H, d, *J* 7 Hz, HO_2C–*H*); *m/e* 336 (M^+, 5%), 290 (11), 208 (36), 123 (57), 109 (34), 95 (30), 83 (64), 81 (42), 69 (32), 55 (33), 43 (100), and 41 (56).

Acetylation of the Hemiacetal (13).—A solution of the hemiacetal (40 mg) in pyridine (2 ml) was mixed with acetic anhydride (1.5 ml), and the mixture was allowed to stand at room temperature for 6 h. The reacted mixture was worked-up as usual to afford as crude product the acetate (14), which was purified by preparative t.l.c. to a viscous liquid; $\nu_{max.}$ (CCl_4) 1 745, 1 710, 1 420, 1 100, 1 045, 1 010, and 940 cm^{-1}; δ 0.75 and 0.84 (each 3 H, d, *J* 7 Hz, Me_2-CH), 1.08 and 1.17 (each 3 H, s, Me–C), 2.13 (3 H, s, OCO-Me), 2.17 (3 H, s, COMe), 4.54 (1 H, m, $W_{\frac{1}{2}}$ 22 Hz, O–C–H), and 5.85 (1 H, d, *J* 8 Hz, O–C(OAc)–*H*); *m/e* 278 (M^+, 1%), 336 (1), 319 (19), 219 (21), 149 (15), 135 (17), 122 (29), 109 (21), 95 (23), 81 (30), 69 (11), 55 (24), 43 (100), and 41 (33).

Pyrolysis of the Acetate (14).—The acetate (70 mg) was heated at 200 °C for 2 h under reduced pressure (2 mmHg). The reacted mixture was developed on a silica gel plate with benzene–hexane–ethanol (10 : 10 : 1), and the main band (R_F 0.64) was collected to give the vinyl ether (15) (35 mg) as a viscous substance, $\nu_{max.}$ (film) 1 700, 1 660, 1 420, 1 240, and 1 160 cm^{-1}; δ 0.83 and 0.91 (each 3 H, d, *J* 7.5 Hz (Me_2CH), 0.98 and 1.05 (each 3 H, s, Me–C), 2.16 (3 H, s, COMe), 2.30—3.00 (4 H, m, 2 × CO–CH_2), 4.08 (1 H, m, $W_{\frac{1}{2}}$ 20 Hz, O–C–H), and 6.22 (1 H, s, =CH–O); *m/e*

318 (M^+, 42%), 303 (10), 275 (11), 245 (36), 217 (26), 176 (21), 151 (21), 123 (30), 109 (29), 108 (30), 91 (37), 81 (40), 69 (40), 55 (32), 43 (100), and 41 (45).

Conversion of the Hemiacetal (14) *into the* 3,4-*Disubstituted Acetophenone* (16).—The hemiacetal (60 mg) was added to a solution of NaOH (100 mg) in a mixture of ethanol (3 ml) and water (1 ml), and the mixture was stirred at room temperature for 3 h. The reacted mixture was poured into water, acidified with dilute HCl and taken up into ether. The reaction product obtained by evaporation of the solvent was purified by preparative t.l.c. using benzene–hexane–ethanol (10 : 10 : 1) to give the 3,4-disubstituted acetophenone (16) (44 mg) as a viscous substance; $[\alpha]_D$ +43.4° (*c* 2.2); $\lambda_{max.}$ (EtOH) 257.5 nm (ε 4 600); $\nu_{max.}$ (film) 1 700, 1 680, 1 600, 1 560, 1 250, 950, and 820 cm^{-1}; δ 0.77 (6 H, d, *J* 7 Hz, Me_2CH), 0.85 (3 H, s, Me–C), 2.06 (3 H, s, COMe), 2.33 (3 H, s, Ar–*Me*), 2.52 (3 H, s, ArCO*Me*), 3.83 (1 H, d, *J* 8 Hz, Ar–C–H), 7.22 (1 H, d, *J* 7 Hz, Ar-H), 7.62 (1 H, dd, *J* 8 and 2 Hz, Ar-H), and 7.87 (1 H, d, *J* 2 Hz, Ar-H); ^{13}C n.m.r. 6 × s; 212.1 and 197.3 (CO); 143.2, 141.5, and 135.0 (substituted aromatic carbons); and 59.1 (tetrasubstituted C); 6 × d: 130.6, 128.3, and 126.1 (aromatic carbons); and 53.2, 48.6, and 31.2 (CH); 2 × t: 38.2 and 27.1 (CH_2); and 6 × q: 26.2, 25.9, 22.0, 21.5, 20.5, and 19.2 (Me); *m/e* 300 (M^+, 7%), 282 (7), 257 (7), 217 (23), 202 (13), 190 (12), 161 (10), 147 (15), 115 (7), 86 (14), 69 (18), 57 (38), 43 (100), and 41 (33).

Structure of (−)-2β-*Acetoxy*-11α-*hydroxyverrucosane* (17).—After the solvent was distilled out, fraction 10 was allowed to stand at room temperature to afford (−)-2β-acetoxy-11α-hydroxyverrucosane (17) (600 mg) in a crystalline state, which was recrystallized from hexane–ether (10 : 1) as colourless needles, m.p. 203—204 °C; $[\alpha]_D$ −103.3° (*c* 2.24); $\nu_{max.}$ (KBr) 3 495, 3 060, 1 707, 1 388, 1 375, 1 260, 1 047, 1 028, and 950 cm^{-1}; *m/e* 348 (M^+, 15), 288 (55), 270 (27), 255 (23), 227 (25), 207 (26), 189 (24), 147 (22), 119 (30), 109 (29), 107 (29), 105 (29), 81 (36), 69 (27), 55 (49), 43 (100), and 41 (65) (Found: C, 75.65; H, 10.55. Calc. for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41%).

Spontaneous hydrolysis of the acetoxy-alcohol (17). The acetoxy-alcohol underwent hydrolysis spontaneously during prolonged storage at room temperature to afford the diol (18), m.p. 132—133 °C; $[\alpha]_D$ −48.8° (*c* 0.58); $\nu_{max.}$ (KBr) 3 460, 3 040, 1 360, 1 380, 1 020, 1 010, 965, and 915 cm^{-1}; δ 0.05—0.06 (3 H, m, cyclopropyl), 0.72, 0.83, 0.91, 0.94, and 1.23 (each 3 H, s, Me–C), 3.65 (1 H, d, *J* 4.4 Hz, HO–C–H), and 3.68 (1 H, d, *J* 9 Hz, HO–C–H).

Acid treatment of the diol (18). The diol (30 mg) was treated with an acetone solution of H_2SO_4 in the manner described for the hydroxy-ketone (3), to furnish the diol (19) (28 mg) as a colourless viscous substance; $[\alpha]_D$ +23.9° (*c* 3.0); $\nu_{max.}$ (KBr) 3 330, 1 030, 1 010, and 980 cm^{-1}; δ 0.88 and 0.86 (each 3 H, d, *J* 6.5, (Me_2CH), 0.74 and 0.89 (each 3 H, s, Me–C), 1.76 (3 H, br s, =C–Me), 3.2—4.05 (2 H, m, HO–C–H), and 5.31 (1 H, br d, *J* 6 Hz, =C–H).

Oxidation of the acetoxy-alcohol (17). The acetoxy-alcohol (90 mg) was dissolved in acetone (3 ml) and stirred together with an excess of Jones reagent at 0 °C for 5 min. The reacted mixture was worked-up as usual to give a viscous substance showing two spots on t.l.c. By preparative t.l.c. using benzene–hexane ethanol (10 : 10 : 1), the less polar component was separated as crystals (34 mg) of the acetoxy-ketone (20), which was recrystallized from hexane–ethyl acetate (20 : 1) as colourless needles, m.p. 135—136 °C; $[\alpha]_D$ −146.8° (*c* 1.1); $\nu_{max.}$ (KBr) 1 735, 1 385, 1 370, 1 230, 1 000, and 940 cm^{-1}; δ 0.2—0.6 (3 H, m, cyclopropyl), 0.81 and 0.84 (each 3 H, d, Me_2CH), 0.83, 0.86, and 1.22 (each 3 H, s, Me–C), 1.97 (3 H, s, OCOMe), and 4.83 (1 H, d, *J* 7.5 Hz, HO–C–H); *m/e* 346 (M^+, 39%), 286 (100), 271 (32), 243 (24), 229 (14), 218 (28), 205 (80), 189 (53), 175 (25), 173 (25), 159 (31), 149 (35), 147 (39), 139 (54), 132 (43), 120 (63), 107 (49), 95 (49), 93 (43), 91 (39), 81 (45), 69 (64), 55 (44), 43 (80), and 41 (48).

The more polar component was separated by preparative t.l.c. to give the diketone (21) as a colourless viscous substance (15 mg); $[\alpha]_D$ −45.5° (*c* 0.59); $\nu_{max.}$ (film) 1 730, 1 700, 1 440, 1 390, 1 380, 1 130, 1 095, and 1 045 cm^{-1}; δ 0.86 and 0.88 (each 3 H, d, *J* 7.5 Hz, Me_2CH), 0.92 and 0.94 (each 3 H, s, Me–C), 1.82 (3 H, s, =C–Me), 2.10 and 2.30 (each 1 H, d, *J* 17 Hz, $COCH_2C$), 2.61 and 3.36 (each 1 H, d, *J* 17 Hz, $=C-CH_2CO$), 2.20—2.70 (2 H, m, $C-COCH_2$), and 5.54 (1 H, br d, *J* 7 Hz, =CH–); *m/e* 302 (M^+, 52%), 287 (10), 259 (23), 245 (11), 230 (12), 216 (16), 205 (27), 173 (24), 163 (41), 137 (37), 121 (37), 107 (39), 96 (100), 81 (38), 69 (47), 55 (41), and 41 (51).

Acid treatment of the acetoxy-ketone (20). A solution of the acetoxy-ketone (30 mg) in acetone (10 ml) was heated with 0.5N-H_2SO_4 (2 ml) under reflux for 2 h. The reacted mixture was treated as described above to give the keto-alcohol (22) as a colourless viscous substance (25 mg) which was purified by preparative t.l.c. using benzene–hexane–ethanol (10 : 10 : 1); $[\alpha]_D$ −37.9° (c 0.84); $\nu_{max.}$ (film) 3 400, 1 730, 1 390, 1 375, 1 020, and 970 cm^{-1}; δ 0.89 and 0.90 (each 3 H, d, *J* 8 Hz, (Me_2CH), 0.89 and 0.98 (each 3 H, s, Me–C), 1.84 (3 H, s, =C–Me), 3.67 (1 H, m, $W_{\frac{1}{2}}$ 24 Hz, HO–C–H), and 5.42 (1 H, br d, *J* 6 Hz); *m/e* 304 (M^+, 21%), 286 (100), 270 (20), 243 (20), 229 (28), 215 (13), 205 (44), 189 (32), 173 (35), 159 (57), 139 (65), 119 (65), 107 (53), 95 (53), 93 (47), 91 (44), 81 (48), 69 (63), 55 (48), and 41 (67).

Decarbonylation of the keto-alcohol (22). The keto-alcohol (50 mg) was mixed with toluene-*p*-sulphonyl hydrazide (55 mg) in methanol (7 ml) and the mixture was allowed to stand at room temperature for 6 h. The solvent was distilled off *in vacuo*, and the residue was dissolved in dioxan (5 ml) and mixed with $NaBH_4$ (100 mg). The mixture, after standing at room temperature for 2 h, was diluted with water, acidified with dilute H_2SO_4, and extracted with ether. After evaporation of solvent, the residue was purified by preparative t.l.c. using benzene–hexane–ethanol (10 : 10 : 1) to give the alcohol (23) as colourless needles (10 mg), m.p. 153—154 °C; $[\alpha]_D$ +17.2° (*c* 0.3). $\nu_{max.}$ (KBr) 3 250, 1 396, 1 387, 1 033, and 980 cm^{-1}; δ 0.87 and 0.88 (each 3 H, Me_2CH), 0.80 and 0.90 (each 3 H, s, Me–C), 1.79 (3 H, br s, =C–Me), 3.46 (1 H, br t, *J* 12 Hz, HO–C–H), and 5.34 (1 H, br d, *J* 5 Hz, =CH); *m/e* 290 (M^+, 7%), 272 (M^+ − 18, 48), 257 (15), 228 (22), 191 (37), 122 (48), 120 (52), 118 (52), 95 (59), 93 (67), 91 (52), 81 (37), 69 (74), 55 (44), 43 (81), and 41 (100) (Found: C, 82.50; H, 11.95. Calc. for $C_{20}H_{34}O$: C, 82.69; H, 11.80%).

Decarbonylation of the keto-alcohol (6). Compound (6) was decarbonylated as described for the keto-alcohol (22). The monoalcohol thus obtained was identical with the monoalcohol (23) in the n.m.r. and i.r. spectra, and showed no mixed m.p. depression.

Structure of (−)-11α-*Acetoxy*-2β-*hydroxyverrucosane* (24).—From fractions 6 and 7, a compound showing one spot, R_F 0.50, on t.l.c. using benzene–hexane–ethanol (10 : 10 : 1) was separated (150 mg). It was recrystallized from hexane–ether to give colourless needles, m.p. 100.7—

102 °C; $[\alpha]_D$ −31.9° (*c* 0.9); $\nu_{max.}$ (KBr) 3 480, 3 040, 1 710, 1 240, 1 030, and 1 020 cm^{-1}; *m/e* 348 (M^+, 1%), 310 (8), 306 (4), 288 (6), 270 (13), 262 (10), 255 (10), 189 (14), 176 (18), 161 (11), 147 (14), 135 (13), 121 (17), 119 (17), 107 (23), 105 (18), 95 (26), 93 (24), 91 (18), 81 (31), 67 (27), 57 (49), 55 (49), 43 (100), and 41 (85) (Found: C, 75.95; H, 10.30. Calc. for $C_{22}H_{36}O_3$: C, 75.81; H, 10.41%).

Acetylation of the acetoxy-alcohol (17). The acetoxy-alcohol (30 mg) was dissolved in pyridine (5 ml) and mixed with acetyl chloride (0.7 ml), and the mixture allowed to stand at room temperature overnight. The reacted mixture was treated in the usual way to give a solid substance which was purified by t.l.c. [benzene–hexane–ethanol (10 : 10 : 1)]. The diacetate (25) (15 mg) thus obtained was recrystallized from ether as colourless needles, m.p. 135—136 °C; $[\alpha]_D$ −99.8° (*c* 0.2); $\nu_{max.}$ (KBr) 3 050, 1 720, 1 230, 1 240, 1 020, and 1 010 cm^{-1}; δ 0.73, 0.82, 0.84, 0.96, and 1.31 (each 3 H, s, Me–C), 2.09 (6 H, s, OCOMe), 4.73 (1 H, d, *J* 4.5 Hz, AcO–C–H), and 5.03 (1 H, d, *J* 9 Hz, AcO–C–H); *m/e* 390 (M^+, 3%), 330 (16), 270 (31), 255 (18), 189 (29), 147 (14), 132 (17), 122 (15), 120 (18), 118 (20), 107 (19), 93 (14), 81 (20), 79 (18), 69 (15), 55 (20), 43 (100), and 41 (28).

Acetylation of the acetoxy-alcohol (24). A solution of the acetoxy-alcohol (80 mg) in pyridine (5 ml) was mixed with acetic anhydride (2 ml) and the mixture was heated under reflux for 48 h. The reacted mixture was worked-up as usual to give a diacetate which was identical with the diacetate (25) (60 mg) on the basis of n.m.r., i.r., and mass spectra; it showed no mixed m.p. depression.

Structure of (−)-2β-*Hydroxyverrucosane* (26).—The compound (2.5 g) was isolated from fractions 2 and 3 as a semi-crystalline substance showing a spot at R_F 0.95 on t.l.c. [benzene–hexane–ethanol (10 : 10 : 1)]. It was purified by preparative t.l.c. and recrystallized from hexane–ether to give colourless needles, m.p. 76.5—78 °C; $[\alpha]_D$ −57.9° (c 1.5); $\nu_{max.}$ (KBr) 3 610, 3 050, 1 380, 1 370, and 1 035 cm^{-1}; *m/e* 290 (M^+, 6%), 272 (M^+ − 18, 22), 229 (11), 191 (22), 124 (14), 107 (30), 95 (35), 93 (31), 69 (42), 55 (51), 43 (47), and 41 (100).

Acid treatment of alcohol (26). The alcohol (40 mg) was dissolved in acetone (10 ml) and heated with 0.5N-H_2SO_4 (2 ml) under reflux for 4 h. The reacted mixture was treated in a usual way to give an alcohol (38 mg) which was identical with the alcohol (23) obtained by decarbonylation of the keto-alcohol (22), on the basis of n.m.r., i.r., and mass spectra; it also showed no mixed m.p. depression.

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