Phytochemistry, Vol. 20, No. 11, pp. 2539–2542, 1981.
Printed in Great Britain.

0031-9422/81/112539-04 $02.00/0

TWO TRITERPENES FROM THE FLOWERS OF *CAMELLIA JAPONICA*

HIDEJI ITOKAWA, HIROYUKI NAKAJIMA, AKIRA IKUTA and YOICHI IITAKA*

Tokyo College of Pharmacy, 1432-1 Horinouchi, Hachioji, Tokyo, Japan; *Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan

(*Received* 28 *January* 1981)

Key Word Index—*Camellia japonica*; Theaceae; triterpene; 28-noroleanane-type; maragenin II; camellenodiol; camelledionol; X-ray crystallography.

Abstract—Two new triterpenoids from the flowers of *Camellia japonica* have been identified as 3β,18β-dihydroxy-28-norolean-12-en-16-one and 18β-hydroxy-28-norolean-12-ene-3,16-dione. A large amount of 3β-hydroxy-28-noroleana-12,17-dien-16-one was also obtained.

INTRODUCTION

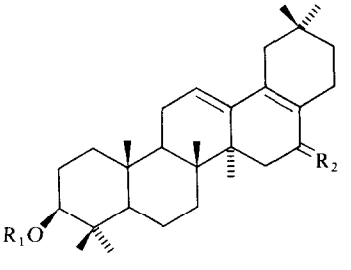
The sapogenins camelliagenin A, B and C [1–4] have been isolated from the fruit of *Camellia japonica* L. In this paper, we report on the isolation and characterization from the flowers of this plant, which have been used in the treatment of haematemesis in Japanese folk medicine, of two new 28-noroleanane-type triterpenes.

RESULTS AND DISCUSSION

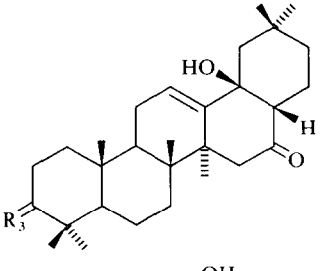
Compound **1a**, $C_{29}H_{44}O_2$, was crystallized from MeOH as colourless needles, mp 228.0–228.5°. The presence in its ^{1}H NMR spectrum of seven sharp singlets (δ 0.80–1.12) for tertiary methyl groups suggested a nortriterpenoid skeleton. There was also a signal for a C-3 proton at δ 3.21 which was shifted to δ 4.48 by acetylation (**1b**). Its UV spectrum showed strong absorption at 299 nm and the IR spectrum contained a band at 1655 cm^{-1} indicative of the presence of an α,β-unsaturated keto group with extended conjugation. Moreover, the ^{1}H NMR and ^{13}C NMR data showed the presence of one olefinic proton at C-12 (δ 6.08, *t*, J = 4 Hz) and four olefinic carbons [δ 126.8 (*s*), 128.9 (*d*), 139.1 (s) and 146.8 (*s*)]. Thus **1a** contained two double bonds, one of which was trisubstituted whilst the other was tetrasubstituted. The MS of **1a** contained ions at *m/z* 189 and 216 (Fig. 1) formed as a result of the retro-Diels–Alder cleavage of rings A/B and D/E. The former ion suggested the presence of the C-3 hydroxyl group and the latter was characteristic of a Δ^{12}-oleanane skeleton [5]. Wolff–Kishner reduction of **1a** gave a deoxy-compound (**2a**, $C_{29}H_{46}O$), the UV absorption (244 nm) of which suggested the presence of a heteroannular diene system (calc. value 244 nm). **2a** was identified as 28-noroleana-12,17-dien-3β-ol by direct comparison of its acetate (**2b**) with an authentic sample of **2b** [6].

From the above facts, we decided that **1a** might be maragenin II, 3β-hydroxy-28-noroleana-12,17-dien-16-one, a compound that had been isolated as its acetate from *Marah macrocarpus* [7]. However, the mp (215–217°, **1b** 187.0–187.5°) and the IR and NMR data (provided by Prof. P. J. Hylands) of maragenin II acetate differed from those of **1a**. To confirm the structure **1a**, its *p*-bromobenzoate (**1c**, $C_{36}H_{47}O_3Br$) was subjected to X-ray analysis. The perspective view of the molecule is shown in Fig. 2 and **1a** was confirmed as maragenin II, a compound that had not been isolated previously from natural sources except as its acetate.

Compound **3a**, $C_{29}H_{46}O_3$, was crystallized from MeOH as colourless needles, mp 215.0–216.5°. Its ^{1}H NMR spectrum contained seven sharp singlets (δ 0.81–1.19) for tertiary methyl groups, suggesting a



1a $R_1 = H$, $R_2 = O$
1b $R_1 = Ac$, $R_2 = O$
1c $R_1 = p$-bromobenzoyl, $R_2 = O$
2a $R_1 = H$, $R_2 = H_2$
2b $R_1 = Ac$, $R_2 = H_2$



3a $R_3 = \overset{OH}{\underset{H}{}}$
3b $R_3 = \overset{OAc}{\underset{H}{}}$
4 $R_3 = O$

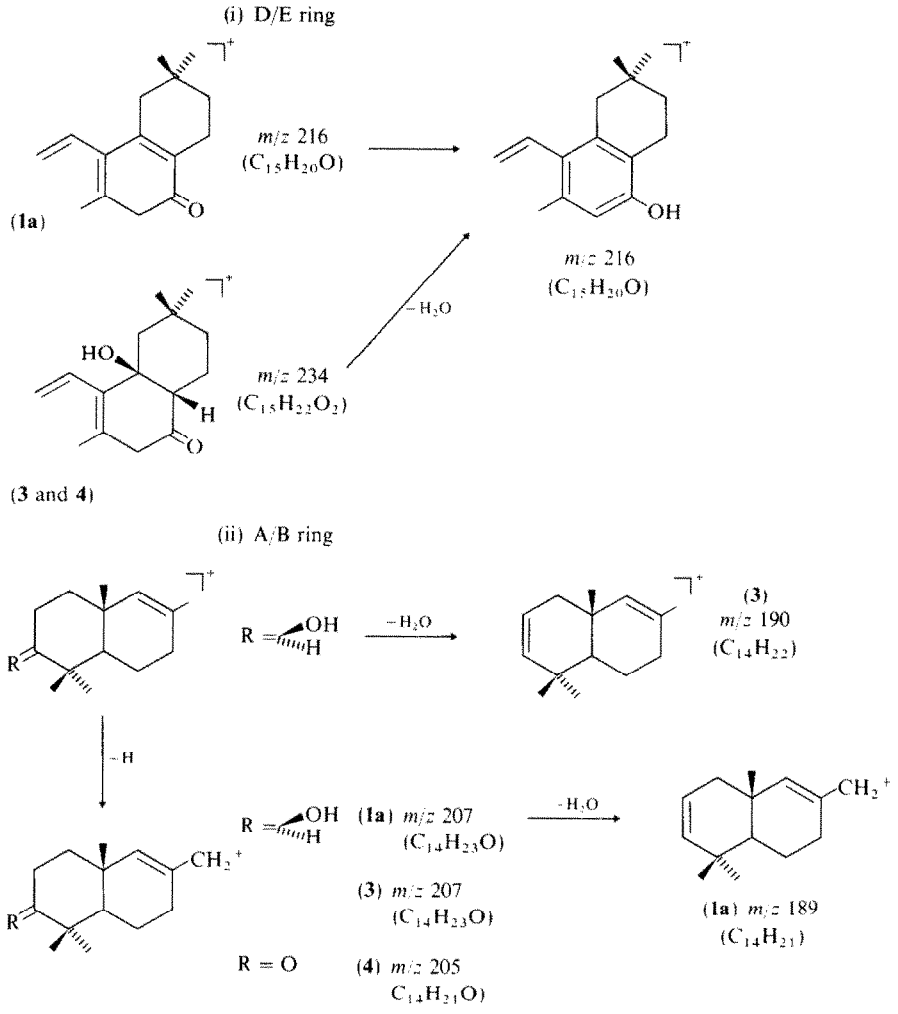


Fig. 1. Fragmentation of A/B and D/E rings of **1a**, **3** and **4**. Elemental values determined by high-resolution MS.

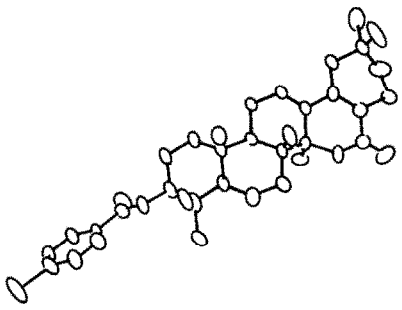


Fig. 2. The molecular structure of **1c**.

nortriterpenoid, and its IR spectrum had a band at 1710 cm^{-1} indicative of a non-conjugated ketone. It gave a monoacetate (**3b**), which still contained a hydroxyl group [IR, 3420 cm^{-1}; ^{13}C NMR, δ 76.5 (*s*)]. This suggested that **3a** contained a tertiary hydroxyl group in addition to a 3β-hydroxyl group. The MS of **3a** like that of **1a** contained ions (*m/z* 234, 216 and 190) formed as a result of retro-Diels–Alder cleavage of rings D/E and A/B, respectively (Fig. 1) [5]. Treatment of **3a** with *p*-toluenesulfonic acid and calcium chloride gave a dehydrated compound which was identified as **1b** by comparison with an authentic sample. Furthermore, the position of the hydroxyl group was determined on the basis of the lower field methine proton signal at δ 2.69 ppm, which could be assigned to the methine proton at C-17 adjacent to the carbonyl group and required the presence of a C-18 hydroxyl group. Thus, **3a** is 3β,18-dihydroxy-28-norolean-12-en-16-one.

Compound **4**, $C_{29}H_{44}O_3$, crystallized from MeOH as colourless crystals, mp 232–233°, and had a similar MS to **3a**, except that the molecular ion peak (*m/z* 440) was two mass units lower. Oxidation of **3a** with chromium trioxide–pyridine reagent gave **4**. Therefore **4** was the 3-one of **3a**, i.e. 18-hydroxy-28-norolean-12-ene-3,16-dione.

The last problem was the stereochemistry at C-18. If the C-18 hydroxyl group was in the α-configuration, it would be expected to cause an unmistakeable downfield shift in the ^1H NMR spectrum of the C-27 methyl group [8,9]. However, both **3a** and **4** showed a sharp singlet at δ 1.19 which could be assigned to the C-27 methyl group and which seemed to have little influence on the hydroxyl

group in comparison with δ1.15 of 3β-hydroxy-28-norolean-12-en-16-one (maragenin I) [7], and this suggested that the C-18 hydroxyl group of **3a** and **4** was in the β-configuration (*cis* D/E). To confirm the *cis* D/E ring junction, we examined the pyridine-induced solvent shifts of **4** on the ^{1}H NMR spectrum. The Δ values ($\Delta = \delta_{CDCl_3} - \delta_{C_5C_5N}$) of the signal of the methine proton at C-17 was $\delta - 0.41$. This strong deshielding indicated a narrow dihedral angle between the proton and the hydroxyl group [10]. The CD curve of **3a** (Fig. 3) showed a negative Cotton effect which also favoured this configuration. **4** showed a more weakly negative Cotton effect which seemed to be due to the influence of the 3-keto group in addition to the 16-one. Inspection of Dreiding models showed that these were the expected Cotton effects. **3a** and **4** are thus 3β,18β-dihydroxy-28-norolean-12-en-16-one and 18β-hydroxy-28-norolean-12-ene-3,16-dione, respectively, with the absolute structures shown in the structural formulae (**3a** and **4**).

3a and **4** are new compounds from natural sources. We propose that they should be called camellenodiol and camelledionol, respectively, after the genus of the plant from which they were isolated.

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR and ^{13}C NMR spectra were measured at 100 MHz and 25 MHz, respectively, in 10 mm tubes with TMS as int. standard.

Isolation **1a**, **3a**, *and* **4**. Dried flowers of *Camellia japonica* (3 kg) were extracted with MeOH. The MeOH extract was concd *in vacuo*, then dissolved in H_2O and partitioned with *n*-BuOH. The *n*-BuOH-soluble fraction was evapd, dissolved in a small amount of MeOH and poured into Et_2O. After removal of the ppt. (contains crude saponins) by filtration, the filtrate was evapd and chromatographed over Si gel with *n*-hexane–EtOAc–MeOH. To the fraction eluted with *n*-hexane–EtOAc (7:3), MeOH was added and the ppt. recrystallized (MeOH–$CHCl_3$) to give **1a** (1.5 g), shining flakes. The filtrate was repeatedly sepd and purified by Si gel CC, prep. TLC ($CHCl_3$–MeOH, 20:1) and HPLC (*n*-hexane–EtOAc, 7:3) to give **3a** (52 mg) and **4** (10 mg) as colourless needles (MeOH) and colourless crystals (MeOH), respectively.

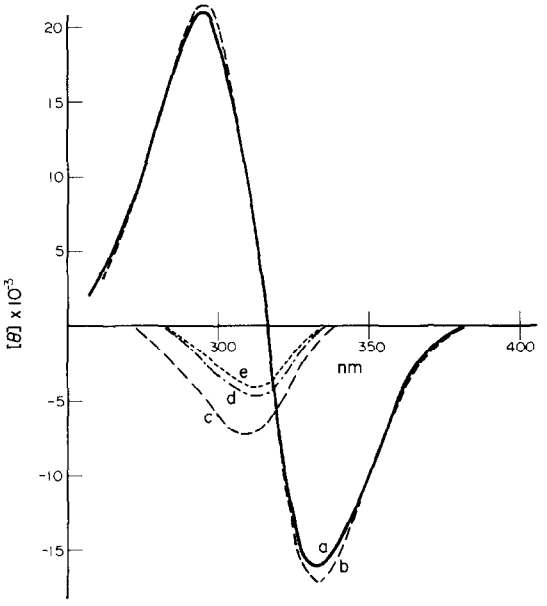


Fig. 3. CD curves of (a) **1b**, (b) the compound formed on dehydration of **3b**, (c) **3a**, (d) **4** and (e) the compound formed by chromic oxidation of **3a**.

3β-Hydroxy-28-noroleana-12,17-dien-16-one (**1a**). Mp 228.0–228.5°. $[\alpha]_D^{18}$ +41° (*c* 0.39, $CHCl_3$). (Found: C, 81.93; H, 10.62. Calc. for $C_{29}H_{44}O_2$: C, 82.02, H, 10.44.) UV λ_{max}^{MeOH} nm (ε): 299 (11 900); IR ν_{max}^{KBr} cm^{-1}: 3350, 2920, 1655, 1450, 1385, 1040; MS *m/z* (rel. int.): 424 [M]$^+$ (45), 216 (39), 207 (10), 204 (100), 203 (34), 189 (18); ^{1}H NMR ($CDCl_3$): δ 0.80 (3 H, *s*), 0.91 (3 H, *s*), 0.95 (6 H, *s*), 0.97 (3 H, *s*), 1.01 (3 H, *s*), 1.12 (3 H, *s*), 3.21 (1 H, *t*-like), 3.46 (1 H, *s*, disappeared with D_2O), 6.08 (1 H, *t*, J = 4 Hz); ^{13}C NMR ($CDCl_3$) (OFR): δ 15.6, 17.9, 18.2, 20.6, 23.1, 24.1, 27.1, 28.1, 28.6, 29.2, 33.4, 36.8, 38.7, 40.4, 44.1, 44.9, 46.1, 55.3, 78.7 (*d*), 126.8 (*s*), 128.9 (*d*), 139.1 (*s*), 146.8 (*s*), 200.4 (*s*).

3β,18β-Dihydroxy-28-norolean-12-en-16-one (**3a**). Mp 215.0–216.5°. $[\alpha]_D^{25}$ +30° (*c* 0.22, $CHCl_3$). M$^+$ 442.3447, calc. for $C_{29}H_{46}O_3$, 442.3446; IR ν_{max}^{KBr} cm^{-1}: 3340, 2920, 1710, 1450, 1385, 1365, 1030; MS *m/z* (rel. int.): 442 [M]$^+$ (4), 424 (6), 409 (3), 234 (77), 216 (100), 207 (42), 190 (34), 175 (14), 149 (14); ^{1}H NMR ($CDCl_3$): δ 0.81 (3 H, *s*), 0.90 (3 H, *s*), 0.98 (6 H, *s*), 1.01 (3 H, *s*), 1.05 (3 H, *s*), 1.19 (3 H, *s*), 2.69 (1 H, *dd*, J = 12, 4 Hz), 3.14 (1 H, *d*, J = 14 Hz), 3.20 (1 H, *t*, J = 8 Hz), 5.46 (1 H, *t*, J = 3 Hz); CD (*c* 0.0058, MeOH): $[\theta]_{340}$ 0°, $[\theta]_{325}$ −3506°, $[\theta]_{310}$ −7315° (pk), $[\theta]_{290}$ −3658°, $[\theta]_{266}$ −304°.

18β-Hydroxy-28-norolean-12-ene-3,16-dione (**4**). Mp 232.0–233.0°. $[\alpha]_D^{26}$ +49° (*c* 0.10, $CHCl_3$). M$^+$ 440.3276, calc. for $C_{29}H_{44}O_3$, 440.3287; IR ν_{max}^{KBr} cm^{-1}: 3430, 2940, 1695, 1460, 1385, 1245; MS *m/z* (rel. int.): 440 [M]$^+$ (2), 411 (5), 234 (70), 216 (100), 206 (15), 205 (18), 201 (14), 191 (21), 149 (35); ^{1}H NMR ($CDCl_3$): δ 0.89 (3 H, *s*), 0.96 (3 H, *s*), 1.06 (3 H, *s*), 1.07 (3 H, *s*), 1.09 (6 H, *s*), 1.19 (3 H, *s*), 2.73 (1 H, *dd*, J = 13, 5 Hz), 3.18 (1 H, *d*, J = 14 Hz), 5.52 (1 H, *t*, J = 4 Hz); ^{1}H NMR (C_5D_5N): 0.92 (3 H, *s*), 0.99 (6 H, *s*), 1.05 (3 H, *s*), 1.17 (3 H, *s*), 1.30 (3 H, *s*), 1.32 (3 H, *s*), 3.14 (1 H, *dd*, J = 14, 5 Hz), 3.73 (1 H, *d*, J = 13 Hz), 5.51 (1 H, *t*, J = 4 Hz); CD (*c* 0.0048, MeOH): $[\theta]_{336}$ 0°, $[\theta]_{325}$ −2567°, $[\theta]_{312}$ −4767° (pk), $[\theta]_{295}$ −2383°, $[\theta]_{282}$ 0°.

Acetylation of **1a**. 1a (300 mg) was acetylated with Ac_2O–pyridine (4 ml, 1:1) at room temp. overnight. The mixture was poured into ice–H_2O and the ppt. was recryst. (MeOH–$CHCl_3$) to give colourless plates (**1b**, 292 mg). Mp 187.0–187.5°; $[\alpha]_D^{26}$ +29° (*c* 0.56, $CHCl_3$); UV λ_{max}^{MeOH} nm (ε) 299 (13 400); IR ν_{max}^{KBr} cm^{-1}: 2920, 1730, 1660, 1450, 1370, 1240, 1030; MS *m/z* (rel. int.): 466 [M]$^+$ (34), 406 (18), 216 (42), 204 (68), 203 (100), 189 (24); ^{1}H NMR ($CDCl_3$): δ 0.90 (6 H, *s*), 0.95 (3 H, *s*), 0.96 (3 H, *s*), 0.97 (3 H, *s*), 1.01 (3 H, *s*), 1.12 (3 H, *s*), 2.06 (3 H, *s*), 4.48 (1 H, *t*-like), 6.08 (1 H, *t*, J = 4 Hz); CD (*c* 0.0043, MeOH): $[\theta]_{385}$ 0°, $[\theta]_{370}$ −1733°, $[\theta]_{350}$ −9320°, $[\theta]_{333}$ −16 256° (pk), $[\theta]_{316}$ 0°, $[\theta]_{296}$ 21 024° (pk), $[\theta]_{270}$ 8450°, $[\theta]_{250}$ 0°.

Wolff–Kishner reduction of **1a**. **1a** (100 mg) was heated for 6 hr with diethylene glycol (6 ml), Na (0.4 g) and dry hydrazine (1.0 ml) in a sealed tube at 200–210°. After cooling, H_2O was added and the product was extrd with $CHCl_3$ and purified by prep. TLC ($CHCl_3$–MeOH, 40:1). Recrystallization (MeOH–EtOAc) gave colourless needles of **2a** (67 mg). Mp 186.0–187.0°; $[\alpha]_D^{23}$ +76° (*c* 0.11, $CHCl_3$); M$^+$ 410.3525, calc. for $C_{29}H_{46}O$, 410.3545; UV λ_{max}^{MeOH} nm (ε): 237 (18 800), 244 (20 400), 252 (sh, 14 600); IR ν_{max}^{KBr} cm^{-1}: 3300, 2950, 1450, 1380, 1040; MS *m/z* (rel. int.): 410 [M]$^+$ (100), 395 (7), 202 (48), 190 (59), 189 (46); ^{1}H NMR ($CDCl_3$): δ 0.80 (3 H, *s*), 0.89 (6 H, *s*), 0.92 (3 H, *s*), 0.99 (6 H, *s*), 1.01 (3 H, *s*), 3.21 (1 H, *t*-like), 5.48 (1 H, *t*, J = 4 Hz); ^{13}C NMR ($CDCl_3$) (OFR): δ 15.7, 16.0, 16.3, 16.8, 18.4, 21.0, 23.5, 27.3, 28.1, 28.3, 28.4, 28.9, 29.3, 29.4, 33.8, 35.2, 37.0, 38.6, 38.8, 39.6, 41.1, 47.3, 55.5, 78.9 (*d*), 116.5 (*d*), 125.2 (*s*), 129.0 (*s*), 140.2 (*s*).

Acetylation of **2a**. **2a** (55 mg) was acetylated with Ac_2O–pyridine (4 ml, 1:1) at room temp. overnight. The mixture was poured into ice–H_2O and the ppt. was recrystallized (MeOH–$CHCl_3$) to give colourless needles of **2b** (52 mg). Mp 187.0–189.0°; $[\alpha]_D^{23}$ +65° (*c* 0.12, $CHCl_3$). UV λ_{max}^{MeOH} nm (ε): 237 (17 300), 244 (18 800), 252 (sh, 13 200); IR ν_{max}^{KBr} cm^{-1}: 2920, 1730, 1240, 1030; MS *m/z* (rel. int.): 452 (100), 437 (11), 392 (4), 377 (6), 215 (11), 202 (36), 190 (41), 189 (47); ^1H NMR ($CDCl_3$): δ 0.88 (12 H, *s*), 0.90 (3 H, *s*), 0.95 (3 H, *s*), 0.96 (3 H, *s*), 2.04 (3 H, *s*), 4.49 (1 H, *t*-like), 5.48 (1 H, *t*, *J* = 4 Hz).

Synthesis and X-ray analysis of **1c**. **1a** (50 mg) and *p*-bromobenzoyl chloride (50 mg) were suspended in pyridine and kept for 3 hr at room temp. The mixture was poured into ice–H_2O and the ppt. was chromatographed over Si gel ($CHCl_3$). Recrystallization (MeOH–EtOAc) gave colourless needles of **1c**. Mp 279.0–280.0°. (Found: C, 71.32; H, 7.79; Br, 13.32. Calc. for $C_{36}H_{47}O_5Br$: C, 71.16; H, 7.80; Br, 13.15). IR ν_{max}^{KBr} cm^{-1}: 2920, 1705, 1660, 1585, 1390, 1270, 1115, 1010, 755; MS *m/z* (rel. int.): 608 $[M+2]^+$ (22), 606 $[M]^+$ (22), 216 (31), 204 (41), 203 (100), 185 (29), 183 (31).

Crystal data. **1c**, $C_{36}H_{47}O_3Br$, MW = 606, monoclinic, space group $P2_1$, *Z* = 2, D_{cal} = 1.272 g/cm^3, *a* = 21.042 (10), *b* = 6.838 (3), *c* = 11.129 (6) Å, β = 99.04 (5)°, *U* = 1581.4 $Å^3$. 1680 independent reflections were observed within 2θ range of 6–155°, out of 2909 theoretically possible reflections. 325 Friedel reflections of the type *hkl* against *hkl* reflections were also observed. The structure was solved by the heavy-atom method and refined by the block-diagonal matrix least-squares method to an *R* value of 0.09 excluding H-atoms. Absolute configuration was determined by using the anomalous dispersion effect of the Br atom for CuK_α radiation. Out of 70 *hkl* and *hkl* pairs, for which more than 6% intensity differences were expected, 62 pairs definitely indicated the absolute configuration shown in Fig. 2.

Acetylation of **3a**. **3a** (25 mg) was acetylated with Ac_2O–pyridine (1 ml, 1:1) at room temp. overnight. H_2O was added and the product was extracted with $CHCl_3$ and chromatographed over Si gel (n-hexane–EtOAc, 9:1). Recrystallization (MeOH) gave colourless plates of **3b** (22 mg). Mp 260.5–261.5°. $[\alpha]_D^{25}$ +24° (*c* 0.20, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3420, 2930, 1720, 1710, 1440, 1365, 1240, 1030; MS *m/z* (rel. int.): 484 $[M]^+$ (2), 466 (3), 424 (3), 406 (2), 249 (6), 234 (75), 216 (100), 190 (63), 175 (19), 149 (15); ^1H NMR ($CDCl_3$): δ 0.90 (9 H, *s*), 0.97 (6 H, *s*), 1.04 (3 H, *s*), 1.18 (3 H, *s*), 2.05 (3 H, *s*), 2.69 (1 H, *dd*, *J* = 12, 4 Hz), 3.13 (1 H, *d*, *J* = 14 Hz), 4.46 (1 H, *t*, *J* = 8 Hz), 5.47 (1 H, *t*, *J* = 3 Hz); ^{13}C NMR ($CDCl_3$) (OFR): δ 15.4, 16.7, 17.3, 18.2, 21.2, 23.5, 23.7, 27.0, 28.1, 30.3, 30.8, 32.3, 32.6, 36.4, 37.0, 37.7, 38.1, 39.9, 43.0, 46.6, 47.2, 47.4, 52.5, 55.4, 76.5 (*s*), 80.8 (*d*), 125.4 (*d*), 140.4 (*s*), 170.8 (*s*), 213.3 (*s*).

Dehydration of **3b**. **3b** (5.4 mg) in C_6H_6 was heated at 50° for 2 hr with *p*-toluenesulfonic acid (2.9 mg) and $CaCl_2$ (5.7 mg). After cooling, the soln was filtered and the filtrate was washed with $NaHCO_3$ soln and chromatographed over Si gel (*n*-hexane–EtOAc, 9:1). The product (1.9 mg) was identified as **1b** by TLC, MS, UV, CD and GLC. UV λ_{max}^{MeOH} nm (ε): 299 (13 060): MS *m/z* (rel. int.): 466 $[M]^+$ (42), 451 (2), 406 (3), 216 (49), 204 (72), 203 (100), 189 (20); CD (*c* 0.0038, MeOH): $[\theta]_{385}$ 0°, $[\theta]_{370}$ −1962°, $[\theta]_{350}$ −9811°, $[\theta]_{333}$ −7046° (pk), $[\theta]_{317}$ 0°, $[\theta]_{297}$ 21 461° (pk), $[\theta]_{270}$ 7358°, $[\theta]_{200}$ 0°.

CrO_3 *oxidation of* **3a**. **3a** (5.0 mg) in pyridine was added to CrO_3–pyridine suspension (5.5 mg: 1 ml). The mixture was kept at room temp. overnight, Et_2O was added and the ppt was filtered off. The filtrate was washed with dil. HCl and chromatographed over Si gel (*n*-hexane–EtOAc 3:1). The product (1.8 mg) was identified as **4** by TLC, MS, CD and GLC. MS *m/z* (rel. int.): 440 $[M]^+$ (3), 422 (9), 407 (5), 234 (58), 216 (100), 206 (23), 205 (18), 201 (16), 191 (22), 149 (41); CD (*c* 0.0090, MeOH): $[\theta]_{338}$ 0°, $[\theta]_{325}$ −2200, $[\theta]_{312}$ −4106° (pk), $[\theta]_{295}$ −1857°, $[\theta]_{282}$ 0°.

Acknowledgements—We wish to thank Dr. P. J. Hylands, University of London, for the spectral data of maragenin II; Dr. K. G. Lewis, University of New England, for the gift of authentic 28-noroleana-12, 17-dien-3β-yl acetate; Y. Shida, S. Suzuki, Mrs. T. Sakuma and Miss K. Matsuda, Central Analytical Laboratory (Tokyo College of Pharmacy) for MS, ^1H NMR, ^{13}C NMR and elemental analysis; and Mrs. F. Hasegawa, Science University of Tokyo, for the measurements of high resolution MS.

REFERENCES

1. Ito, S., Kodama, M. and Konoike, M. (1967) *Tetrahedron Letters* 591.
2. Itokawa, H., Sawada, N. and Murakami, T. (1967) *Tetrahedron Letters* 597.
3. Itokawa, H., Sawada, N. and Murakami, T. (1968) *Yakugaku Zasshi* **88,** 1463.
4. Itokawa, H., Sawada, N. and Murakami, T. (1969) *Chem. Pharm. Bull.* **17,** 474.
5. Budzikiewicz, H., Wilson, J. M. and Djerassi, C. (1963) *J. Am. Chem. Soc.* **85,** 3688.
6. Hensens, O. D. and Lewis, K. G. (1971) *Aust. J. Chem.* **24,** 2117.
7. Hylands, P. J. and Salama, A. M. (1979) *Tetrahedron* **35,** 417.
8. Kawazoe, Y., Sato, Y., Natsume, M., Hasegawa, H., Okamoto, T. and Tsuda, K. (1962) *Chem. Pharm. Bull.* **10,** 338.
9. Ito, S., Kodama, M., Sunagawa, M. and Oba, T. (1969) *Tetrahedron Letters* 2905.
10. Demarco, P. V., Farkas, E., Doddrell, D., Mylari, B. L. and Wenkert, E. (1968) *J. Am. Chem. Soc.* **90,** 5480.