Phytochemistry, 1978, Vol 17 pp. 1975–1978 ©Pergamon Press Ltd. Printed in England 0031-9422/78/1101-1975 $02.00/0

A NEW TRITERPENE GLUCOSIDE FROM *CYMBIDIUM GIGANTEUM**

JAN DAHMÉN and KURT LEANDER

Department of Organic Chemistry, Arrhenius Laboratory, University of Stockholm, S-106 91 Stockholm, Sweden

(*Received* 10 *May* 1978)

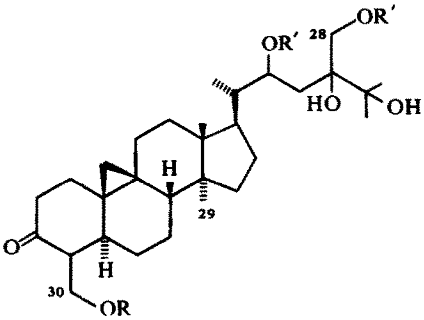
Key Word Index—*Cymbidium giganteum*; Orchidaceae; triterpene glucoside; cymbidoside.

Abstract—A new triterpene glucoside, cymbidoside, has been isolated from *Cymbidium giganteum*. Its structure is shown to be 4ξ-(β-D-glucopyranosyloxymethyl)-14α-methyl-22ξ, 24ξ, 25, 28-tetrahydroxy-9,19-cyclo-5α,9β-ergostan-3-one.

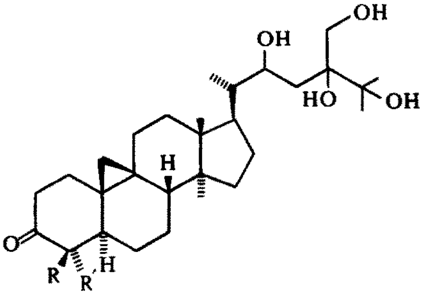
A glucoside, named cymbidoside, was isolated from *Cymbidium giganteum* Wall. by gel permeation on Sephadex LH-20 followed by chromatography on Si gel. Spectral and elemental analyses of cymbidoside (**1**) and its corresponding aglycone (**2**) indicated that **1** had the molecular formula $C_{36}H_{60}O_{11}$. Sugar [2, 3] and methylation [4] analyses showed **1** to be a glucopyranoside. On enzymatic hydrolysis with β-D-glucosidase from almonds, **1** gave the corresponding aglycone **2**, named cymbidosone. This result, together with the large coupling constant (7.5 Hz) of the anomeric proton in the ^1H NMR spectrum of **1**, showed that cymbidoside (**1**) is a β-D-glucopyranoside.

On treatment of cymbidoside (**1**) with aqueous NaOH in THF the α,β-unsaturated ketone **4** was rapidly produced, thereby establishing the position of the sugar moiety. Hydrogenation of cymbidoside (**1**) in aqueous NaOH–THF with palladium as a catalyst gave the methyl derivative **5**.

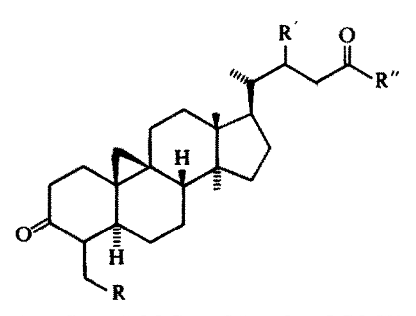
On treatment with acetic anhydride–pyridine, cymbidosone (**2**) formed the triacetate **3**, the ^1H NMR spectrum of which, compared with that of **2** showed one of the acetylated hydroxyl functions to be secondary and the other two primary. Oxidation of **3** with HIO_4 in ether [5] gave the diketone **6**. On treatment with HIO_4, cymbidosone (**2**) rapidly consumed one equivalent of the reagent to give the diketone **7** and then, if an excess of the reagent was used, an acid which was not characterized. In an analogous manner, the ketone **5** was oxidized with an excess of HIO_4 in ether, and when the oxidation was followed by methylation with diazomethane the methyl ester **8** was obtained. Dehydration of **8** using $POCl_3$ in pyridine gave the α,β-unsaturated ester **14**, which on hydrogenation in ethyl acetate with palladium as a catalyst gave the saturated compound **9**. Reduction of the 3-keto function in **9** with $NaBH_4$ in methanol produced the two epimeric alcohols **10** and **11** in the ratio of 2:1. Acetylation of **10** and **11** with acetic anhydride–pyridine gave the corresponding acetates **12** and **13**. The map and ^1H NMR data of **12** are in agree-



1 R = β-D-glucopyranosyl; R' = H
2 R = R' = H
3 R = R' = $COCH_3$



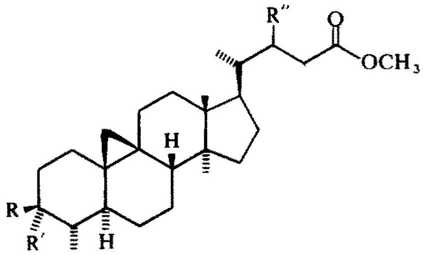
4 R,R' = CH_2
5 R = H; R' = CH_3



6 R = R' = $OCOCH_3$; R'' = CH_2OCOCH_3
7 R = R' = OH; R'' = $COH(CH_3)_2$

---

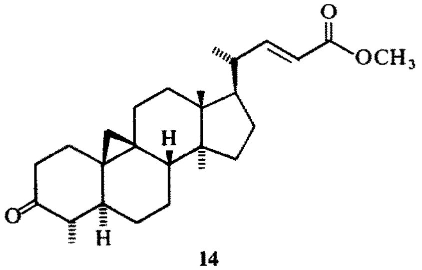
* Part 8 in the series "Studies on Orchidaceae Glycosides". For part 7 see ref. [1].



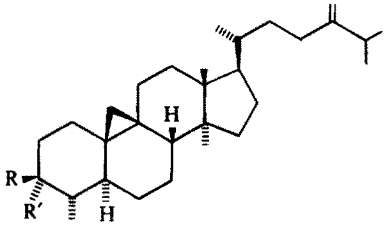
8 R,R' = O; R'' = OH
9 R,R' = O; R'' = H
10 R = OH; R' = R'' = H
11 R = H; R' = OH; R'' = H
12 R = OCOCH$_3$; R' = R'' = H
13 R = H; R' = OCOCH$_3$; R'' = H

ment with those reported [6] for methyl 3β-acetoxy-4α,14α-dimethyl-25,26,27,28-tetranor-9,19-cyclo-5α,9β-ergostan-24-oate derived from cycloeucalenol (**15**). From these results it is evident that cymbidosone must be 4ξ-(β-D-glucopyranosyloxymethyl)-14α-methyl-22ξ, 24ξ, 25,28-tetrahydroxy-9,19-cyclo-5α,9β-ergostan-3-one.

^{13}C NMR spectra were reorded for the compounds **2**, **3**, **5**, **7**, **8** and **14** (Table 1). The assignments of the carbon resonances were made on the basis of those reported [7] for cycloeucalenone (**16**) together with off-resonance measurements. The chemical shifts for the relevant carbon atoms throughout the degradation series are in good agreement with those reported for **16** except for those for C-7 and C-16 for which the assignments in **16**, on the basis of the results here obtained should probably be reversed (i.e. C-7 δ 26.9 and C-16 δ 28.0 ppm).



14



15 R = OH; R' = H
16 R,R' = O

Table 1. ^{13}C NMR shifts in ppm

	2	**7**	**3**	**5**	**8**	**14**	**16**
C-1	32.1	32.2	32.7	32.8	32.8	32.8	32.8
C-2	41.3	41.3	41.0	40.9	40.9	40.9	40.8
C-3	212.0	211.9	209.6	213.5	213.0	212.7	212.2
C-4	57.7	57.7	54.2	50.0	49.9	50.0	49.8
C-5	40.5	40.5	41.6	46.0	46.0	46.0	45.9
C-6	25.3	25.4	25.1	25.2	25.2	25.2	25.1
C-7	27.2	27.0	27.1	27.0	26.9	27.0	28.0
C-8	47.4	47.4	47.1	47.1	47.0	47.1	46.9
C-9	24.8	24.8	25.1	24.9	24.9	24.8	24.9
C-10	28.8	28.9	28.9	29.3	29.3	29.4	29.3
C-11	25.8	25.8	25.6	25.9	25.8	25.9	25.8
C-12	35.8	35.8	35.4	35.5	35.5	35.5	35.3
C-13	45.9	46.0	45.7	45.7	45.8	45.8	45.2
C-14	48.6	48.5	48.4	48.4	48.4	48.9	48.7
C-15	33.0	32.9	32.7	32.7	32.7	32.7	32.8
C-16	27.7	27.5	26.5	27.3	27.1	28.2	26.9
C-17	49.6	49.7	49.1	49.2	49.0	51.3	52.1
C-18	18.2	18.2	18.1	17.9	17.9	18.1	17.9
C-19	26.8	26.8	26.9	27.1	27.1	27.1	27.1
C-20	43.9	43.0	39.7	42.8	41.0	40.2	36.0
C-21	12.6	12.7	12.3	12.0	12.0	18.8	18.3
C-22	69.4	69.7	73.3	69.5	69.7	155.1	35.0
C-23	34.2	38.0	30.8	33.4	35.0	118.7	31.3
C-24	77.5	216.6	75.2	76.5	174.2	167.3	156.1
C-25	75.3	77.1	75.1	75.3	—	—	33.7
C-26	26.1	27.0	24.9	24.9	—	—	21.8
C-27	26 1	27.0	24.8	24.6	—	—	21.8
C-28	66.1	—	66.6	65.9	—	—	105.6
C-29	19.5	19.5	19.3	19.3	19.3	19.2	19.1
C-30	57.5	57.6	59.8	10.8	10.7	10.8	10.7
CH_3O	—	—	—	—	51.8	51.3	—
$\underline{C}H_3CO$	—	—	21.6	—	—	—	—
	—	—	20.9	—	—	—	—
	—	—	20.9	—	—	—	—
$CH_3\underline{C}O$	—	—	170.1	—	—	—	—
	—	—	170.8	—	—	—	—
	—	—	170.8	—	—	—	—

Solvents: compounds **2** and **7** in C_5D_5N, compounds **3**, **5**, **8**, **14** and **16** in $CDCl_3$.

EXPERIMENTAL

Mps are corr. Elemental analyses were carried out at Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany. Plates precoated with Si gel F_{254} (Merck) were used for TLC and spots were visualized by spraying with H_2SO_4 (8%) followed by heating to 120°.

Plant material. Cymbidium giganteum Wall. was delivered from Mr. N. Prakash, Chandra Orchid and Bulb Nurseries, 8.5 miles P.O. Kalimpong, West Bengal, India.

Isolation of cymbidoside (**1**). The green parts of fresh plants of *C. giganteum* (5.8 kg) were extracted with MeOH (22 l.) and the soln was concd to 1 l. A part (0.85 l.) of this extract was diluted with H_2O (0.85 l.) and washed with $CHCl_3$ (5 × 200 ml). The aq. layer was saturated with BuOH and extracted with BuOH saturated with H_2O (5 × 200 ml). The butanolic phase was washed with H_2O saturated with BuOH (70 ml) and evapd to dryness. A part (5.2 g) of the residue (10.3 g) was filtered through a column of Sephadex LH-20 (7.5 × 57 cm) using EtOH–H_2O (1:1) as eluent. The fraction (1.25 g) containing **1** (R_f 0.8, $CHCl_3$–MeOH–H_2O, 65:35:10 lower phase) was chromatographed on Si gel (5 × 12 cm) using $CHCl_3$–EtOH (2:1) as eluent to give crude **1**. Recrystallization 2 × from *iso*-PrOH–H_2O gave **1** (325 mg). Needles, mp 150–152°, $[\alpha]^{22}_{578}$ +24° (*c* 1.5, MeOH). (Found: C, 63.1; H, 8.7; O, 28.0. $C_{36}H_{60}O_{11}$. 1 H_2O requires: C, 63.0; H, 9.1; O, 28.0%). IR ν^{KBr}_{max} cm^{-1}: 3700–3000 (s), 1700 (s). ^{1}H NMR (C_5D_5N + D_2O): δ 0.30 (*d*, 1H, *J* = 4 Hz), 0.49 (*d*, 1H,

$J = 4$ Hz), 0.83 (*s*, 3H), 1.03 (*s*, 3H), 1.25 (*d*, 3H, $J = 6$ Hz), 1.72 (*s*, 6H), 3.80–4.84 (11H), 4.99 (*d*, 1H, $J = 7.5$ Hz).

Preparation of cymbidosone (**2**) A suspension of cymbidoside (**1**, 260 mg) and β-D-glucosidase from almonds (260 mg) in a mixture of potassium hydrogen phthalate buffer soln (pH 5.25, 75 ml) and MeOH (3 ml) was stirred at 37° for 4 days. The mixture was saturated with BuOH and extracted with BuOH saturated with H_2O (5 × 20 ml). The butanolic phase was evapd to dryness. Chromatography on Si gel (2.6 × 16 cm) using $CHCl_3$–MeOH (9·1) as eluent gave **2** (141 mg). Needles (EtOH), mp 226–229° (d): $[\alpha]^{22}_{578}$ +28° (*c* 1.2, C_5H_5N). (Found: C, 71.4; H, 9.8; O, 18.8. $C_{30}H_{50}O_6$ requires: C, 71.1; H, 10.0; O, 18.9 %). IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1}: 3620–3100 (s), 3055 (w), 1695 (s). ^{1}H NMR ($CDCl_3$ + D_2O): δ 0.43 (*d*, 1H, $J = 4$ Hz), 0.63 (*d*, 1H, $J = 4$ Hz), 0.90 (*s*, 3H), 0.92 (*d*, 3H, $J = 6$ Hz), 1.04 (*s*, 3H), 1.23 (*s*, 3H), 1.26 (*s*, 3H), 3.65 and 3.76 (AB pattern, 2H, $J = 12$ Hz), 3.69 and 3.87 (AB part of an ABX system, 2H, $J_{AB} = 12$ Hz, $J_{AX} = 3$ Hz, $J_{BX} = 6$ Hz), 4.13 (*d*, 1H, further coupled, $J = 10$ Hz). Ms, *m/e* (rel. int.): 506 (M^+, 0.2), 488 (1), 470 (3), 457 (2), 452 (2), 439 (3), 411 (2), 370 (2), 335 (3), 344 (5), 326 (3), 315 (5), 297 (6), 201 (7), 187 (8), 175 (14), 173 (13), 161 (13), 159 (13), 149 (13), 145 (100), 127 (27), 101 (43), 95 (32), 81 (28), 73 (28), 59 (33), 55 (28), 43 (53).

Acetylation of cymbidosone (**2**). Cymbidosone (**2**) was treated with an excess of Ac_2O–Py (1:1) at room temp. for 18 hr. The reaction mixture was evapd to give **3** as an amorphous solid $[\alpha]^{21}_{578}$ +38° (*c* 0.7, $CHCl_3$). IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1}: 3600–3200 (m), 1730 (s, *br*). ^{1}H NMR ($CDCl_3$): δ 0.42 (*d*, 1H, $J = 4$ Hz), 0.65 (*d*, 1H, $J = 4$ Hz), 0.88 (*d*, 3H, $J = 6$ Hz), 0.91 (*s*, 3H), 1.01 (*s*, 3H), 1.27 (*s*, 6H), 2.03 (*s*, 6H), 2.09 (*s*, 3H), 2.2–2.6 (3H), 4.06 and 4.20 (AB pattern, 2H, $J = 12$ Hz), 4.15–4.50 (2H), 5.26 (*d*, 1H, further coupled, $J = 8$ Hz).

Oxidation of **3** *with* HIO_4. **3** (13 mg) was dissolved in Et_2O (1 ml) and a saturated soln of $HIO_4 \times 2\,H_2O$ in Et_2O was added dropwise at room temp. until the starting material was absent (HIO_4 consumed: 0.02 mmol). The reaction was followed by TLC ($CHCl_3$–MeOH, 19:1, R_f **3** 0.4, R_f **6**: 0.7). The reaction mixture was filtered, evapd and the residue was chromatographed on Si gel (1.5 × 17 cm) using $CHCl_3$–MeOH (19:1) as eluent to give **6** as an amorphous solid. $[\alpha]^{21}_{578}$ +38° (*c* 1.1, $CHCl_3$). IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1}: 1740 (s), 1715 (s). ^{1}H NMR ($CDCl_3$): δ 0.44 (*d*, 1H, $J = 4$ Hz), 0.66 (*d*, 1H, $J = 4$ Hz), 0.91 (*d*, 3H, $J = 6$ Hz), 0.92 (*s*, 3H), 1.02 (*s*, 3H), 2.02 (*s*, 6H), 2.17 (*s*, 3H), 4.16–4.38 (2H), 4.68 (*s*, 2H), 5.36 (*d*, 1H, further coupled, $J = 9$ Hz).

Oxidation of **2** *with one equiv*. HIO_4. Cymbidosone (**2**, 12.8 mg) was dissolved in THF (13 ml) and a saturated soln of $HIO_4 \times 2\,H_2O$ in Et_2O was added dropwise during 20 min (amount HIO_4 added: 0.025 mmol). The reaction was followed by TLC ($CHCl_3$–MeOH, 9:1, R_f **2**: 0.3, R_f **7**: 0.6). The reaction mixture was diluted with Et_2O (2 ml), washed with saturated $NaHCO_3$ soln and then with H_2O. The etheral layer was dried (Na_2SO_4), filtered and evapd to give crude **7**. Chromatography on Si gel (0.7 × 16 cm) using $CHCl_3$–MeOH (9:1) as eluent gave **7** (8.2 mg). Needles (MeOH–H_2O), mp 189–191°; $[\alpha]^{21}_{578}$ +54° (*c* 0.6, $CHCl_3$). IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1}: 3600–3000 (m), 3030 (w), 1715 (s). ^{1}H NMR ($CDCl_3$ +D_2O): δ 0.44 (*d*, 1H, $J = 4$ Hz), 0.65 (*d*, 1H, $J = 4$ Hz), 0.91 (*s*, 3H), 0.94 (*d*, 3H, $J = 6$ Hz), 1.05 (*s*, 3H), 1.40 (*s*, 6H), 3.69 and 3.89 (AB part of an ABX system, 2H, $J_{AB} = 12$ Hz, $J_{AX} = 3$ Hz, $J_{BX} = 6$ Hz), 4.19 (*dt*, 1H, $J_1 = 9$ Hz, J_2, $J_3 = 3$ Hz).

Preparation of **4**. Cymbidoside (**1**, 56 mg) was dissolved in a mixture of THF (3.5 ml) and H_2O (2.5 ml). NaOH (2M, 0.15 ml) was added and the mixture was kept at 35° for 15 min and then neutralized (HCl, 2M). The THF was evapd and the residue was extracted with Et_2O (5 × 1 ml). The Et_2O phase was dried (Na_2SO_4) and evapd to give crude **4**. PLC on Si gel using CH_3CN–toluene (4:5) as eluent and eluting the gel with EtOAc gave **4** (29 mg) as an amorphous solid (if MeOH was used as eluent another compound was obtained which, according to its ^{1}H NMR spectrum, should be a MeOH adduct). $[\alpha]^{21}_{578}$ +78° (*c* 0.8, $CHCl_3$). IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1}: 3620–3120 (m), 1690 (s), 1615 (m). UV $\lambda^{\mathrm{EtOH}}_{\mathrm{max}}$ nm (ε): 314 (29), 226.5 (3827). ^{1}H NMR ($CDCl_3$): δ 0.33 and 0.38 (AB pattern, 2H, $J = 4$ Hz), 0.92 (*d*, 3H, $J = 7$ Hz), 0.96 (*s*, 3H), 1.04 (*s*, 3H), 1.24 (*s*, 3H), 1.26 (*s*, 3H), 3.69 and 3.79 (AB pattern, 2H, $J = 11.5$ Hz), 4.14 (*d*, 1H, further coupled, $J = 10$ Hz), 5.04 (*dd*, 1H, $J_1 = 2$ Hz, $J_2 = 1.5$ Hz), 5.86 (*dd*, 1H, $J_1 = 2$ Hz, $J_2 = 1.5$ Hz).

Preparation of **5**. Cymbidoside (**1**, 80 mg) was dissolved in a mixture of THF (5.5 ml) and H_2O (1 ml) and NaOH (0.5M, 0.5 ml) was added. This mixture was hydrogenated over Pd (66 mg, 10 % on C) at room temp. and atm pres. for 30 min. The reaction was followed by TLC ($CHCl_3$–MeOH–H_2O, 65:35:10 lower phase and $CHCl_3$–MeOH, 9:1). After neutralization (HCl, 1M), the mixture was filtered and evapd. PLC on Si gel using toluene–EtOAc–MeOH (4:10:1) as eluent gave **5** (38 mg). Needles (MeOH–H_2O), mp 193–196°; $[\alpha]^{21}_{578}$ +56° (*c* 0.9, $CHCl_3$). IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1}: 3500 (m), 3360 (m), 3180 (m), 3035 (w), 1710 (s). ^{1}H NMR ($CDCl_3$): δ 0.41 (*d*, 1H, $J = 4$ Hz), 0.63 (*d*, 1H, $J = 4$ Hz), 0.91 (*s*, 3H), 0.92 (*d*, 3H, $J = 6$ Hz). 0.99 (*d*, 3H, $J = 7$ Hz), 1.04 (*s*, 3H), 1.24 (*s*, 3H), 1.26 (*s*, 3H), 3.69 and 3.79 (AB pattern, 2H, $J = 11.5$ Hz), 4.16 (*d*, 1H, further coupled, $J = 10$ Hz).

Oxidation of **5** *with an excess of* HIO_4. **5** (23 mg) was dissolved in THF (2.5 ml) and a slight excess of $HIO_4 \times 2\,H_2O$ in Et_2O was added. The reaction was followed by TLC ($CHCl_3$–MeOH, 9:1) After being stirred at room temp. for 80 min the reaction mixture was filtered, diluted with Et_2O (10 ml) and extracted with saturated $NaHCO_3$ soln. The aq. layer was washed with Et_2O, acidified (HCl, 2M) and extracted with Et_2O. Methylation with an excess of CH_2N_2 in Et_2O followed by chromatography on Si gel (1.4 × 12 cm) using $CHCl_3$–MeOH (9:1) as eluent gave crude **8**. Crystallization from hexane–Et_2O at −20° gave **8** (10 mg). Needles, mp 145–148°; $[\alpha]^{21}_{578}$ +43° (*c* 0.6, $CHCl_3$). IR $\nu^{\mathrm{KBr}}_{\mathrm{max}}$ cm^{-1}: 3520 (m), 3420–3280 (m), 3040 (w), 1745 (s), 1715 (s). ^{1}H NMR ($CDCl_3$): δ 0.40 (*d*, 1H, $J = 4$ Hz), 0.63 (*d*, 1H, $J = 4$ Hz), 0.90 (*s*, 3H), 0.90 (*d*, 3H, $J = 6.5$ Hz), 0.99 (*d*, 3H, $J = 7$ Hz), 1.04 (*s*, 3H), 3.73 (*s*, 3H), 4.02–4.25 (*m*, 1H).

Preparation of **14**. **7** (10 mg) was dissolved in Py (1.5 ml) and $POCl_3$ (0.05 ml) was added. The reaction mixture was kept at room temp. for 2 hr and then poured into H_2O and extracted with Et_2O. The ethereal layer was dried (Na_2SO_4) and evapd to give **14** (4.7 mg). Needles (MeOH), mp 153–156°; $[\alpha]^{21}_{578}$ +60° (*c* 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.63 (*d*, 1H, $J = 4$ Hz), 0.75 (*d*, 1H, $J = 4$ Hz), 0.91 (*s*, 3H), 0.99 (*d*, 3H. $J = 6.5$ Hz), 1.05 (*s*, 3H), 1.06 (*d*, 3H, $J = 6$ Hz), 3.73 (*s*, 3H), 5.78 (*d*, 1H, $J = 15.5$ Hz), 6.87 (*dd*, 1H, $J_1 = 15.5$ Hz, $J_2 = 8.5$ Hz).

Preparation of **9**. **14** was hydrogenated at room temp. and atm pres. in EtOAc for 3 hr with Pd (10 % on C) as a catalyst, filtered and evapd to give **9**. Needles (MeOH–H_2O), mp 135–136.5°; $[\alpha]^{21}_{578}$ +58° (*c* 0.4, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.40 (*d*, 1H, $J = 4$ Hz), 0.62 (*d*, 1H, $J = 4$ Hz), 0.89 (*d*, 3H, $J = 6$ Hz), 0.91 (*s*, 3H), 0.99 (*d*, 3H, $J = 6.5$ Hz), 1.01 (*s*, 3H), 3.67 (*s*, 3H).

Reduction of **9** *with* $NaBH_4$. **9** (5.5 mg) was dissolved in MeOH (2.5 ml) and $NaBH_4$ (1 mg) was added. The reaction mixture was kept at room temp. for 45 min, acidified with HOAc and evapd. MeOH was added and the soln was evapd again. This procedure was repeated 2 ×. PLC on Si gel using Et_2O–petrol (1:3) as eluent (the plate was developed 3 ×) gave **10** (3.2 mg) and **11** (1.8 mg).

Characterization of **10**. Needles (MeOH–H_2O), mp 158–160°; $[\alpha]^{21}_{578}$ +46° (*c* 0.3, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.14 (*d*, 1H, $J = 4$ Hz), 0.38 (*d*, 1H, $J = 4$ Hz), 0.88 (*d*, 3H, $J = 5$ Hz), 0.89 (*s*, 3H), 0.97 (*s*, 3H), 0.98 (*d*, 3H, $J = 5$ Hz), 3.08–3.36 (1H, *br*), 3.64 (*s*, 3H).

Characterization of **11**. Needles (MeOH–H_2O), mp 131–124: $[\alpha]^{21}_{578}$ +31° (*c* 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.10 (*d*, 1H, $J = 4$ Hz), 0.37 (*d*, 1H, $J = 4$ Hz), 0.90 (*s*, 3H), 0.94 (2 superimposed doublets, (6H, $J = 7$ Hz), 0.97 (*s*, 3H), 3.40–3.56 (1H, *br*), 3.67 (*s*, 3H).

Acetylation of **10** *and* **11**. **10** and **11** were acetylated and worked up as in the acetylation of **2** to give the acetates **12** and **13**, respectively.

Characterization of **12**. Plates (MeOH–H_2O), mp 126.5–129°; (Lit. [6] mp 124–126°). $[\alpha]^{21}_{578}$ +48° (*c* 0.2, $CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.15 *d*, 1H, $J = 4$ Hz), 0.40 (*d*, 1H, $J = 4$ Hz), 0.84 (2 superimposed doublets, 6H, $J = 6$ Hz), 0.89 (*s*, 3H), 0.96 (*s*, 3H), 2.06 (*s*, 3H), 3.67 (*s*, 3H), 4.36–4.48 (1H *br*).

Characterization of **13**. Needles (MeOH–H_2O), mp 105–110°: $[\alpha]^{21}_{578}$ +2° (*c* 0.1, $CHCl_3$). ^1H NMR ($CDCl_3$): δ 0.12 (*d*, 1H, $J = 4$ Hz), 0.37 (*d*, 1H, $J = 4$ Hz), 0.84 (*d*, 3H, $J = 6$ Hz), 0.88 (*d*, 3H, $J = 6$ Hz), 0.92 (*s*, 3H), 0.97 (*s*, 3H), 2.09 (*s*, 3H). 3.67 (*s*, 3H), 4.94–5.08 (1H, *br*)

Acknowledgements—We thank Dr. Björn Lüning for his interest in this work, Dr. Toshiaki Nishida for valuable discussions and Dr. James C. Schmidt for providing us some original data from the work (ref. [6]) of the late Professor S. Morris Kupchan and Dr. Keith S. Brown Jr. We also thank Professor Gabor Lukacs for a generous gift of cycloeucalenol. Support from the Swedish Natural Science Research Council is gratefully acknowledged.

REFERENCES

1. Dahmén, J. and Leander, K. (1976) *Phytochemistry* **15**, 1986.
2. Sawardecker, J. S., Sloneker, J. H. and Jeanes, A. R. (1965) *Analyt. Chem.* **37**, 1620.
3. Chizhov, O. S., Golovkina, L. S. and Wulfsson, N. S. (1966) *Bull. Acad. Sci. U.S.S.R.* **11**, 1853.
4. Björndahl, H., Hellerquist, C. G., Lindberg, B. and Svensson, S. (1970) *Angew. Chem. Int. Ed. Engl.* **9**, 610.
5. Fieser, L. F. and Fieser, M. (1967) in *Reagents for Org. Synthesis* p. 817. John Wiley, New York.
6. Brown, K. S., Jr. and Kupchan, S. M. (1964) *J. Am. Chem. Soc.* **86**, 4424.
7. Khuong-Huu, F., Sangare, M., Chari, V. M., Bekaert, A., Devys, M., Barbier, M. and Lukacs, G. (1975) *Tetrahedron Letters*, 1787.