Phytochemistry, Vol. 32, No. 5, pp. 1261–1265, 1993
Printed in Great Britain.

0031-9422/93 $6.00+0.00

TERPENOIDS AND STEROLS FROM THE WOOD OF *ABIES PINSAPO*

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(*Received* 6 *May* 1992)

Key Word Index—*Abies pinsapo*; Pinaceae; wood; labdane diterpenoids; cyclolanostanolides; sterols.

Abstract—From the neutral fraction of the hexane extract of the wood of *Abies pinsapo* 11 sesquiterpenoids, seven diterpenoids, three triterpenoids and two sterols have been identified. Three of them are new natural products: 3β-hydroxy-13-epimanool, (23*R*,25*R*)-3α-methoxy-9,19-cyclo-9β-lanostan-26,23-olide and (22*S*)-5α-ergostane-3α,22-diol. Their structures were established by spectroscopic methods and chemical correlations.

INTRODUCTION

In the course of our investigations on different species of the genus *Abies* which grow in southern Spain and northern Africa, we reported the occurrence of sesquiterpene acids related to juvabione in *A. pinsapo* [1] and of diterpenoids and cyclolanostanolides in *A. marocana* [2, 3]. Now we describe the chemical composition of the neutral fraction of the hexane extract from the wood of *A. pinsapo*. We have characterized 11 sesquiterpenoids, three of them juvenile hormone analogues, seven diterpenoids, three triterpenoids and two sterols. Compounds **1**, **5** and **7** are new natural products and their structures have been confirmed by chemical correlations.

RESULTS AND DISCUSSION

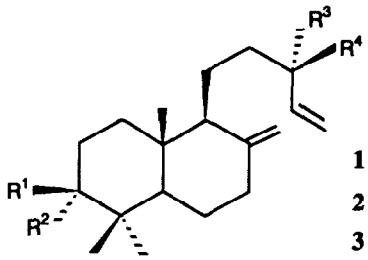
The hydrocarbon fraction was studied by GC-MS. The sesquiterpenoids α-cubebene, cubenene, longifolene, α-murolene, δ-cadinene, *cis*-calamenene [4] and the diterpenoids abieta-7,13-diene [5] and abieta-8,11,13-triene [6] have been identified.

By the usual spectroscopic techniques, the sesquiterpenoids γ-cadinene, germacrene D, epijuvabione, $\Delta^{4'}$-dehydroepijuvabione and epijuvabiol have been characterized. It is remarkable that all the juvenile hormone analogues isolated from *A. pinsapo* and *A. marocana* belong to the *epi*-series [7]. The diterpenoids, **1**, 13-epimanool (**2**) and, after acetylation, 18-acetoxyabieta-7,13-diene, 18-acetoxyabieta-8,11,13-triene and 18-acetoxy-15-hydroxy-abieta-8,11,13-triene have been found, as well as the triterpenoids **5**, (23*R*,25*R*)-3α-hydroxy-9,19-cyclo-9β-lanostan-26,23-olide (**6**) and (23*R*)-3α-hydroxy-9,19-cyclo-9β-lanost-24-en-26,23-olide, and sterol **7** and sitosterol.

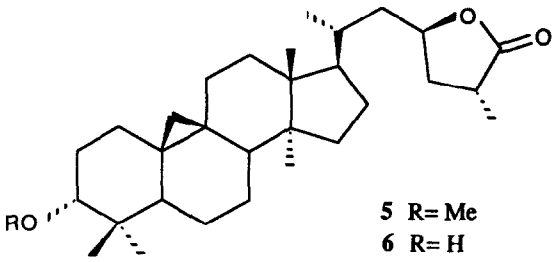
The IR, ^{1}H NMR, ^{13}C NMR and mass spectral data of **1** were in agreement with a structure of hydroxymanool. An *S*-configuration at C-13, similar to that of 13-epimanool (**2**) isolated from the plant, was established by comparison of their ^{1}H NMR spectra (Table 1), recorded at 300 MHz, with the one of manool (**3**), prepared by selective dehydration of sclareol. The signal of H-17a appeared at δ4.51 and 4.50 in **1** and **2**, respectively, whereas it was at δ4.46 in **3**. The other hydroxyl group was located at C-3 due to the upfield chemical shift of C-2, C-3 and C-4 and to the downfield shifts of C-1, C-5, C-18 and C-19 in relation to manool in the ^{13}C NMR spectrum [8]. An equatorial disposition was assigned to this group because H-3 resonated in the ^{1}H NMR spectrum as a double doublet (J_1 = 4.5 Hz, J_2 = 11.6 Hz) at δ3.22. With regard to the absolute stereochemistry, *ent*-3α-hydroxy-13-epimanool, isolated from *Croton sublyratus* [9], presented a negative optical rotation, whereas **1** had $[\alpha]_D$ +17.6°. Thus, **1** must be 3β-hydroxy-13-epimanool. To confirm the structure, **1** was treated with CrO_3–pyridine to give the ketone **4** (IR: 1704 cm^{-1}) which by Huang-Minlon reduction gave a product identical with **2**.

The structure of **5** was assigned by comparison of its spectral data with those of **6**, isolated by us in *A. marocana* [3]. The main differences were that in the IR spectrum of **5** there was no band of a hydroxyl group and in the ^{1}H NMR spectrum (Table 2) a singlet of a methoxyl group at δ3.30 was observed. A pseudotriplet signal (J = 2.2 Hz) at δ2.84 was attributed to the proton in an equatorial disposition and geminal to that oxygenated function. The ^{13}C NMR spectrum (Table 3) showed the signal of the methoxyl group at δ 57.29. The signals of the carbons corresponding to the A ring were shifted in accordance with the change at C-3 from a hydroxyl group in **6** to a methoxyl one in **5**. The similarity for the side chains, in the ^{1}H NMR and ^{13}C NMR spectra, indicated the same configurations at the C-23 and C-25. Therefore, **5** has the structure (23*R*,25*R*)-3α-methoxy-9,19-cyclo-9β-lanostan-26,23-olide.

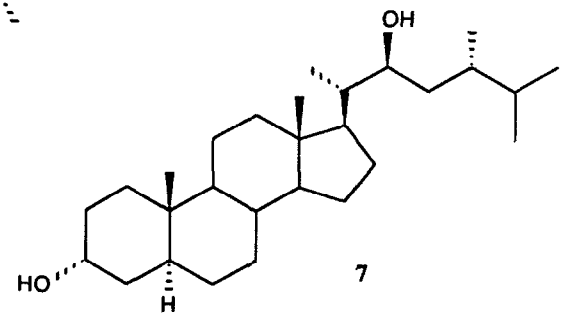
Compound **7** showed in its mass spectrum the molecular peak at *m/z* 418, which, together with the ^{1}H and ^{13}C NMR spectral data, were in agreement with a molecular formula $C_{28}H_{50}O_2$. The IR spectrum showed bands of a hydroxyl group at 3600, 3459 and 1115 cm^{-1} and the



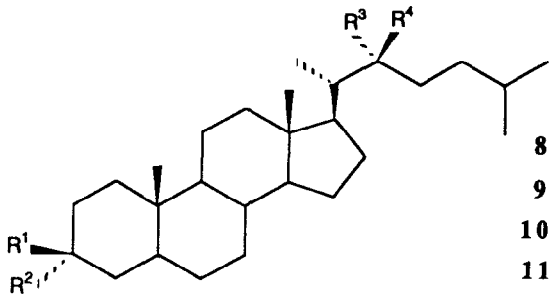
1 $R^1=R^3=$ OH, $R^2=$ H, $R^4=$ Me
2 $R^1=R^2=$ H, $R^3=$ OH, $R^4=$ Me
3 $R^1=R^2=$ H, $R^3=$ Me, $R^4=$ OH
4 $R^1,R^2=$ O, $R^3=$ OH, $R^4=$ Me



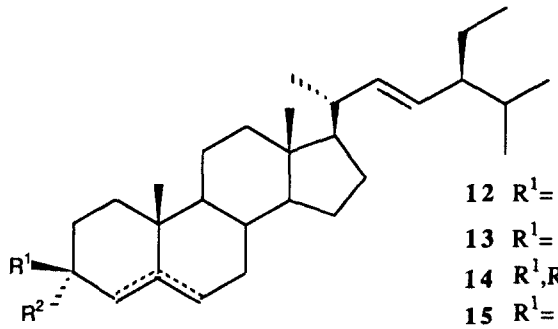
5 R= Me
6 R= H



7



8 $R^1=R^3=R^4=$ H, $R^2=$ OH
9 $R^2=R^3=R^4=$ H, $R^1=$ OH
10 $R^1=$ OOCPh, $R^2=R^3=$ H, $R^4=$ OH
11 $R^1=$ OOCPh, $R^2=R^4=$ H, $R^3=$ OH



12 $R^1=$ H, $R^2=$ OH
13 $R^1=$ OH, $R^2=$ H, Δ^5
14 $R^1,R^2=$ O, Δ^4
15 $R^1=$ OH, $R^2=$ H
16 $R^1=$ H, $R^2=$ OOCPh

signals of the ^{1}H NMR (Table 2) and ^{13}C NMR (Table 3) spectra were consistent with the structure of a dihydroxyergostane. The signals for the carbons of the A ring, in the ^{13}C NMR spectrum, were similar to those of 5α-cholestan-3α-ol-(**8**) and very different to 5α-cholestan-3β-ol (**9**) (Table 3) [10]. This α-disposition of the hydroxyl group at C-3 was supported by the ^{1}H NMR spectrum, where H-3 resonated as a pseudotriplet ($J=2.6$ Hz) at δ4.03 since H-3 was at a similar angle to H-2 and H-4. With respect to the other hydroxyl group, the ^{13}C NMR data were comparable with the ones of the 22-hydroxycholesterol derivatives **10** and **11** [11] (Table 3), with the predictable differences due to the existence of an additional carbon at C-24 in **7**. The signals of C-17, C-20

Table 1. ^{1}H NMR spectral data for compounds **1**–**4** ($CDCl_3$, TMS, 300 MHz)

H	1	2	3	4 (80 MHz)
3	3.22 *dd* (4.5, 11.6)			
14	5.88 *dd* (10.7, 17.4)	5.90 *dd* (10.7, 17.4)	5.90 *dd* (10.7, 17.4)	5.90 *dd* (10.7, 17.4)
15a	5.02 *dd* (1.3, 10.7)	5.03 *dd* (1.3, 10.7)	5.03 *dd* (1.3, 10.7)	5.03 *dd* (1.3, 10.7)
15b	5.18 *dd* (1.3, 17.4)	5.19 *dd* (1.3, 17.4)	5.19 *dd* (1.3, 17.4)	5.19 *dd* (1.3, 17.4)
16	1.25 *s*	1.26 *s*	1.26 *s*	1.26 *s*
17a	4.51 *d* (1.4)	4.50 *d* (1.5)	4.46 *d* (1.4)	4.63 *sa*
17b	4.81 *d* (1.4)	4.80 *d* (1.5)	4.80 *d* (1.4)	4.80 *sa*
18	0.96 *s*	0.85 *s*	0.85 *s*	1.08 *s*
19	0.74 *s*	0.78 *s*	0.78 *s*	1.02 *s*
20	0.66 *s*	0.66 *s*	0.66 *s*	0.87 *s*

Coupling constants (J in Hz) are given in parentheses.

and C-21 were closer to those of **10**, which had a 22*S*-configuration. The multiplicity of H-22 (*t*, $J = 6.4$ Hz), in the ^{1}H NMR spectrum, could be explained assuming free rotation to C-22/C-23 and a preferred conformation where H-20 was at 90° to H-22. The *S*-configurations were proposed for C-20 and C-24, because they are the usual ones for sterols isolated from plants [12]. Thus, a structure of (22*S*)-5α-ergostane-3α,22-diol was assigned for **7**. In order to corroborate the structure proposed for the cyclic system of **7**, compound **12** was prepared starting from stigmasterol (**13**). Oppenauer oxidation of **13** gave the α,β-unsaturated ketone **14** (IR: 1656 cm^{-1}; ^{1}H NMR: δ5.70, *sa*, H-4), which by Birch reduction [13] yielded **15**, that presented in its ^{1}H NMR spectrum (Table 2) a broad multiplet corresponding to H-3α (δ3.60, $W_{1/2} = 20$ Hz). Mitsunobu reaction of **15**, with DEAD. Ph_3P and $PhCO_2H$ [14] gave the benzoate ester **16**, with inverted configuration at C-3 (δ5.30, *m*, $W_{1/2} = 8$ Hz, H-3β). Saponification of **16** with KOH in refluxing methanol generated **12** whose ^{1}H (Table 2) and ^{13}C NMR (Table 3) spectral data agreed with those of **7** for the cyclic system.

Table 2. ^{1}H NMR spectral data for compounds **5**, **7**, **12**, **14**–**16** ($CDCl_3$, TMS)*

H	5	7	12	14	15	16
3	2.84 *pt*† (2.2)	4.03 *pt* (2.6)	4.02 *pt* (2.5)	—	3.60 *m* ($W_{1/2} = 20$ Hz)	5.30 *m* ($W_{1/2} = 8$ Hz)
4	—	—	—	5.70 *sa*	—	—
18	0.90 *s*	0.65 *s*	0.66 *s*	0.70 *s*	0.68 *s*	0.70 *s*
19	0.32 *d* (4.4)	0.76 *s* —	0.77 *s* —	1.21 *s* —	0.81 *s* —	0.87 *s* —
19b	0.48 *d* (4.4)	— —	— —	— —	— —	— —
21	0.92 *d* (7.9)	0.85 *d* (6.8)	1.00 *d* (6.6)	1.01 *d* (6.5)	1.01 *d* (6.0)	1.04 *d* (6.0)
22	— —	3.75*t* (6.4)	5.00 *dd* (8.5, 15.2)	5.08 *pt* (6.0)	5.07 *pt* (6.0)	5.10 *pt* (6.0)
23	4.63 *m* —	— —	5.14 *dd* (8.5, 15.2)	5.08 *pt* (6.0)	5.07 *pt* (6.0)	5.10 *pt* (6.0)
25	2.67 *sext* (7.6)	— —	— —	— —	— —	— —
26	— —	0.79 *d* (6.6)	0.78 *d*[a] (6.4)	0.78 *d*[a] (6.0)	0.79 *d*[a] (6.0)	0.83 *d*[a] (6.0)
27	1.25 *d* (7.3)	0.79 *d* (6.6)	0.83 *d*[a] (6.4)	0.83 *d*[a] (6.0)	0.84 *d*[a] (6.0)	0.88 *d*[a] (6.0)
28	0.94 *s* —	0.83 *d* (7.2)	— —	— —	— —	— —
29	0.84 *s* —	— —	0.79 *t* (7.4)	0.79 *t* (7.0)	0.81 *t* (7.0)	0.87 *t* (7.0)
30	0.84 *s*	—	—	—	—	—
OMe	3.30 *s*	—	—	—	—	—
Ar-*o*	—	—	—	—	—	7.50 *m*
Ar-*m*	—	—	—	—	—	8.07 *m*
Ar-*p*	—	—	—	—	—	7.50 *m*

*5, 7, 12: 300 MHz; 14, 15, 16: 80 MHz.

†*pt*: pseudotriplet.

[a]Interchangeable values.

Coupling constants (J in Hz) are given in parentheses.

Table 3. ^{13}C NMR spectral data for compounds **5**, **7**–**12** (75 MHz, $CDCl_3$, TMS)

C	5	7	8	9	10	11	12
1	27.9[a]	32.2	32.2	37.0	38.2±0.1		32.3
2	23.4	29.1	29.1	31.5	28.0±0.2		29.1
3	86.8	66.7	66.5	71.4	74.5±0.1		66.7
4	39.8	36.0	35.9[a]	38.2	37.0±0.1		36.0
5	41.8	39.2	39.1	44.9	139.7±0.2		39.3
6	21.0	28.6	28.6	28.8	122.6±0.1		28.7
7	25.6[b]	32.0	32.0	32.1	31.9±0.1		32.1
8	48.2	35.6	35.5	35.5	31.9±0.1		35.6
9	19.6	54.3	54.3	54.4	50.0±0.1		54.5
10	26.5	36.1	36.1	35.5	36.6±0.1		36.2
11	26.3	20.9	20.8	21.3	21.1±0.1		20.9
12	33.0	40.1	40.1	40.1	39.8±0.1		40.1
13	45.4	42.6	42.6	42.6	42.3±0.2		42.6
14	49.0	56.5	56.5	56.5	56.4±0.3		56.8
15	35.5	24.2	24.2	24.3	24.2±0.2		24.4
16	28.2[a]	27.9	28.2	28.3	28.1±0.2		29.0
17	52.8	52.7	56.2	56.3	52.6	53.2	56.2
18	18.1	12.1	12.1	12.1	11.8	11.9	12.4
19	30.0	11.3	11.2	12.3	19.4±0.1		11.3
20	33.1	39.4	35.8[a]	35.8	40.3	42.6	40.6
21	18.2	11.3	18.7	18.7	11.6	12.5	19.1
22	42.8	71.8	36.2	36.2	73.8	74.0	129.3
23	76.1	39.4	23.9	23.9	33.3	27.5	138.5
24	36.5	35.4	39.5	39.5	35.7	36.1	51.3
25	34.2	32.1	28.0	28.0	27.8	27.9	32.0
26	180.3	17.9	22.5	22.6	22.6	22.5	21.2
27	16.0	20.1	22.8	22.8	22.6	22.9	21.3
28	26.0	15.9	—	—	—	—	25.5
29	21.5	—	—	—	—	—	12.4
30	19.3	—	—	—	—	—	—
OMe	57.3	—	—	—	—	—	—

Compounds **8**, **9**: ref. [10]. Compounds **10**, **11**: ref. [11].
[a,b]Interchangeable values.

EXPERIMENTAL

The wood was collected in July in Sierra Bermeja (Málaga, Spain) and was identified by Professor F. Valle (Departamento de Biología Vegetal, Universidad de Granada). The air-dried material (9.7 kg) was processed as in ref. [1], yielding 17.8 g of neutral fraction. This was chromatographed under pressure on a silica gel column eluting with hexane–Et_2O mixtures. The least polar fraction was analysed by GC-MS [3], identifying α-cubebene, cubenene, longifolene, α-murolene, δ-cadinene, *cis*-calamenene, abieta-7,13-diene and abieta-8,11,13-triene, on the basis of their R_t and MS. Further chromatographies on silica gel columns yielded the pure compounds, in order of increasing polarity: γ-cadinene (20 mg), germacrene D (104 mg), 13-epimanool (**2**) (800 mg), epijuvabione (98 mg), $\Delta^{4'}$-dehydroepijuvabione (820 mg), **5** (320 mg), 18-acetoxyabieta-7,13-diene (349 mg), 18-acetoxyabieta-8,11,13-triene (41 mg), sitosterol (1.6 g), (23*R*,25*R*)-3α-hydroxy-9,19-cyclo-9β-lanostan-26,23-olide (**6**) (148 mg), (23*R*)-3α-hydroxy-9,19-cyclo-9β-lanost-24-en-26,23-olide (59 mg), epijuvabiol (85 mg), **1** (80 mg), **7** (20 mg) and 18-acetoxy-15-hydroxyabieta-8,11,13-triene (20 mg). The acetyl compounds were obtained after acetylation with Ac_2O in pyridine.

3β-Hydroxy-13-epimanool (**1**). Eluted with hexane–Et_2O (7:3). Syrup; $[\alpha]_D$ +17.6°($CHCl_3$; *c* 3.32); IR ν_{max}^{film} cm^{-1}: 3403, 3082, 2933, 2869, 1711, 1641, 1454, 1408, 1382, 1257, 1180, 1114, 1088, 1032, 1007, 919, 891, 756; ^{13}C NMR (75 MHz, $CDCl_3$): δ (C-1 to C-20) 37.08, 27.93, 78.92, 39.16, 54.69, 24.00, 38.20, 148.05, 57.04, 39.60, 17.88, 41.33, 73.58, 145.27, 111.67, 27.71, 106.97, 28.35, 15.45 and 14.49; EIMS (probe) 70 eV, *m/z* (rel. int.): 289 (1), 288 (4) $[M-H_2O]^+$, 273 (7), 260 (6), 136 (13), 135 (74), 121 (23), 109 (26), 107 (39), 95 (29), 93 (45), 81 (43), 79 (36), 71 (54), 55 (53), 43 (100).

Oxidation of compound **1**. A mixture of CrO_3 (120 mg), pyridine (1.2 ml) and H_2O (0.12 ml) was added to **1** (56 mg). The reaction was allowed to stand for 22 hr with stirring. Work-up as usual gave 38 mg of 3-oxo-13-epimanool (**4**). Syrup; IR ν_{max}^{film} cm^{-1}: 3467, 3081, 2934, 2869, 1704, 1642, 1454, 1384, 1260, 1165, 1109, 997, 917, 803, 754.

Huang–Minlon reduction of compound **4**. A mixture of **4** (38 mg), 80% hydrazine-hydrate (0.1 ml), diethyleneglycol

col (1.5 ml) and KOH (90 mg) was heated at 150–160° for 1 hr and at 240–250° for 1.5 hr under a N_2 atm, followed by usual work-up to give 25 mg of 13-epimanool (**2**). $[\alpha]_D$ +46.4° ($CHCl_3$; *c* 0.70).

(23*R*,25*R*)-3α-*Methoxy*-9,19-*cyclo*-9β-*lanostan*-26,23-*olide* (**5**). Eluted with hexane–Et_2O (9:1). Solid, mp 170–171° (MeOH); $[\alpha]_D$+35.2° ($CHCl_3$; *c* 1.06); IR ν_{max}^{KBr} cm^{-1}: 2937, 2869, 1764, 1454, 1380, 1359, 1300, 1226, 1205, 1178, 1105, 1062, 1030, 998, 946, 924, 899, 648; EIMS (probe) 70 eV, *m/z* (rel. int.): 471 (3), 470 (9) $[M]^+$, 455 (10), 439 (15), 438 (44), 423 (32), 395 (23), 203 (31), 187 (26), 175 (63), 147 (46), 133 (44), 121 (57), 119 (58), 107 (70), 105 (71), 99 (79), 55 (92), 43 (100), 41 (91).

(22*S*)-5 α-*Ergostane*-3 α,22-*diol* (**7**). Eluted with hexane–Et_2O (7:3). Solid, mp 234–235° (CH_3OH); $[\alpha]_D$ +11.8° ($CHCl_3$; *c* 0.48); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3459, 2931, 2870, 1458, 1380, 1240, 1165, 1115, 1000, 970, 902, 822; EIMS (probe) 70 eV, *m/z* (rel. int.): 418 (1) $[M]^+$, 401 (3), 400 (9), 385 (3), 305 (15), 304 (64), 286 (25), 234 (76), 233 (39), 215 (39), 165 (27), 135 (30), 121 (29), 109 (34), 107 (49), 95 (49), 81 (60), 71 (59), 55 (77), 43 (100).

Oppenauer oxidation of stigmasterol (**13**). A soln of Al isopropoxide (7.4 g) in dry C_6H_6 (50 ml) was added to a soln of **13** (10 g) in dry Me_2CO (70 ml) and dry C_6H_6 (95 ml). The mixture was stirred at reflux for 8 hr under a N_2 atm, followed by usual work-up. After repeating the reaction with a further 4.4 g of **13**, both reaction products were combined and chromatographed on a silica gel column. Elution with hexane–Et_2O (17:3) yielded 9.5 g of (22*E*)-stigmasta-4,22-dien-3-one (**14**). Solid, mp 125–127° (hexane); $[\alpha]_D$+57.4° ($CHCl_3$; *c* 0.70); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2957, 2869, 1656, 1611, 1457, 1416, 1378, 1331, 1274, 1229, 1212, 1187, 1113, 1017, 974, 933, 866, 685.

Birch reduction of compound **14**. A soln of **14** (2.5 g) in dry Et_2O (75 ml) was added to a soln of Li (2.5 g) in ammonia (250 ml) and absolute EtOH (35 ml) at −78°. The mixture was stirred at the same temp. for 4.5 hr. Then NH_4Cl (2.5 g) was added and the NH_3 was allowed to evaporate at room temp. The reaction was carried out several times, followed by usual work-up. From 9 g of **13**, 7.6 g of crude were obtained and chromatographed on a silica gel column. Elution with hexane–Et_2O (13:7) gave 4.5 g of (22*E*)-5α-stigmast-22-en-3β-ol (**15**). Solid, mp 160–161°(hexane); $[\alpha]_D$+6.1° ($CHCl_3$; *c* 0.90); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3605, 2932, 2867, 1601, 1459, 1381, 1280, 1169, 1075, 1032, 974, 958, 693.

Mitsunobu reaction of compound **15**. A soln of **15** (2 g), Ph_3P (2.5 g) and $PhCO_2H$ (1.16 g) in dry THF (60 ml) was stirred at room temp. A soln of diethyl azodicarboxylate (DEAD) (1.66 g) in dry THF (10 ml) was added dropwise. After 16 hr the solvent was evapd under red. pres. After repeating the process with 2.5 g of **15**, both crudes were chromatographed on a silica gel column. Elution with hexane–Et_2O (97:3) yielded 4.2 g of (22*E*)-5α-stigmast-22-en-3α-ol benzoate (**16**). Solid, mp 105–106° (hexane); $[\alpha]_D$+2.4° ($CHCl_3$; *c* 1.02); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2934, 2868, 1705, 1601, 1583, 1499, 1381, 1349, 1328, 1314, 1279, 1255, 1175, 1162, 1116, 1070, 1027, 975, 896, 868, 714, 693.

Saponification of compound **16**. A soln of 1M KOH–MeOH (2 ml) was added to **16** (106 mg). After 6 hr at reflux with stirring, the usual work-up yielded 70 mg of a crude that by prep. TLC, eluting with hexane–Et_2O (1:1), gave 46 mg of (22*E*)-5α-stigmast-22-en-3α-ol (**12**). Solid, mp 201–203° (hexane); $[\alpha]_D$+4.3° ($CHCl_3$; *c* 0.75); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3611, 3454, 2931, 2868, 1717, 1452, 1376, 1242, 1163, 1114, 1030, 1000, 975, 903, 825, 696.

Acknowledgement—We wish to thank Professor F. Valle (Departamento de Biología Vegetal, Facultad de Ciencias, Universidad de Granada) for identification of the plant material.

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