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3β-ACETOXYHOPAN-1β,22-DIOL, A TRITERPENE FROM THE LICHEN *PSEUDOPARMELIA TEXANA**

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Key Word Index—*Pseudoparmelia texana*; Parmeliaceae; lichen; 3β-acetoxyhopan-1β,22-diol; triterpene.

Abstract—From the lichen *Pseudoparmelia texana* the triterpene 3β-acetoxyhopan-1β,22-diol has been isolated and its structure elucidated.

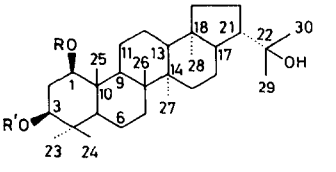
INTRODUCTION

During our studies on the chemistry of lichens we investigated *Pseudoparmelia texana* from the Venezuelan Andes and found, in the benzene extract of this species, in addition to the depside divaricatic acid, a new triterpene, the structural elucidation of which we describe in this report.

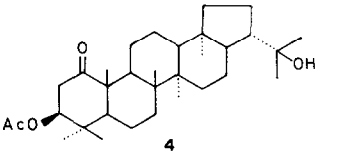
RESULTS AND DISCUSSION

The triterpene (**1**) had mp 273–275° and according to the high resolution mass spectrum the formula was $C_{32}H_{54}O_4$ (found 502.4038; calc. 502.4022). The optical rotation could not be determined because **1** was extremely insoluble in the common solvents. The IR spectrum, with strong bands at 1260, 1702, 3500 and 3620 cm^{-1}, revealed the presence of an acetoxy group and two hydroxyl groups. Acetylation of **1** with acetic anhydride–pyridine at 100° gave an acetate (**2**) with the formula $C_{34}H_{56}O_5$ (MS, found 544.4112; calc. 544.4127) which made likely the presence of one tertiary hydroxyl group. Saponification of **1** yielded the triol, **3**, $C_{30}H_{52}O_3$, mp 246–248° and $[\alpha]_D^{24}$ + 6°, not identical with any of the known triterpenes from lichens. Oxidation of **1** with Sarett's reagent led to the ketone, **4**, which on saponification with potassium hydroxide–methanol lost the elements of water with the formation of the α,β-unsaturated ketone, **5**, with UV λ_{max} 226 nm (log ε 3.87; in methanol) in excellent agreement with the UV spectrum of allo-betul-2-en-1-one [1] with UV λ_{max} 226 nm (log ε 3.94; in methanol). Hydrogenation of **5** with Adams' catalyst yielded the ketol, **6**. Treatment of **4** and **6** with acetic acid–sulphuric acid gave the hop-17(21)-enes, **7** and **8**, respectively.

The mass spectra of **1**–**6** showed fragments at *m/z* 207, 189 and 149 (Scheme 1) typical of 22-hydroxyhopanes [2] and suggested that the other two oxygen functions were attached to C-1 and C-3 of ring A of the hopane skeleton. A vicinal position of the hydroxyl groups could be excluded because the triol, **3**, did not react with periodate.



	R	R'
1	H	Ac
2	Ac	Ac
3	H	H



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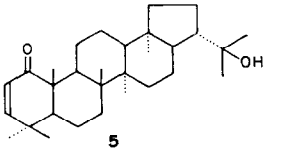

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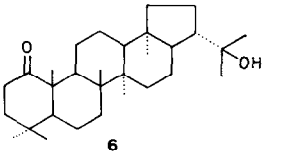

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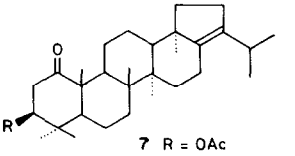
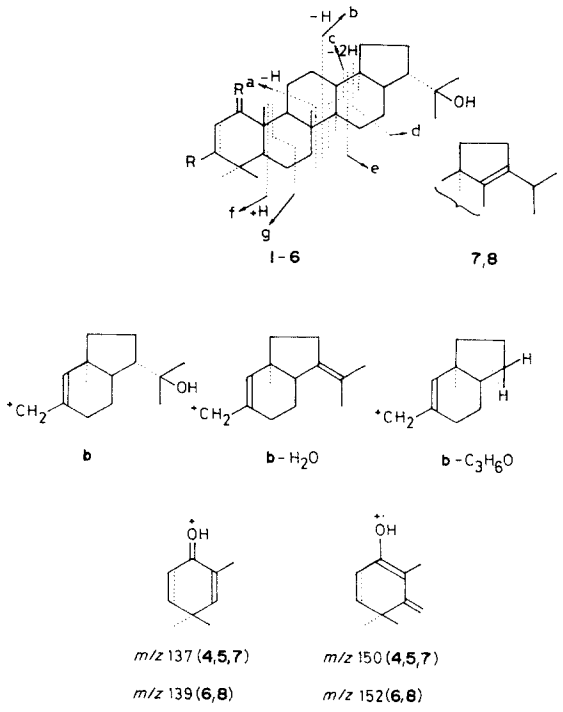


7 R = OAc
8 R = H

*Part 136 in the series "Lichen Substances". For Part 135 see Huneck, S. and John, V. *Herzogia* (submitted).



Scheme 1. Mass spectral fragmentation of the hopanes, **1**–**8**.

The ORD spectra of **4**, **6** and **5** were in very good agreement with the ORD spectra of allo-betul-1-one and allo-betul-2-en-1-one, respectively, proving position C-1 of the keto group in **4**, **5** and **6** (Fig. 1).

The final proof of the structure and stereochemistry of **1**–**8** came from the ^{1}H NMR and ^{13}C NMR spectra. The

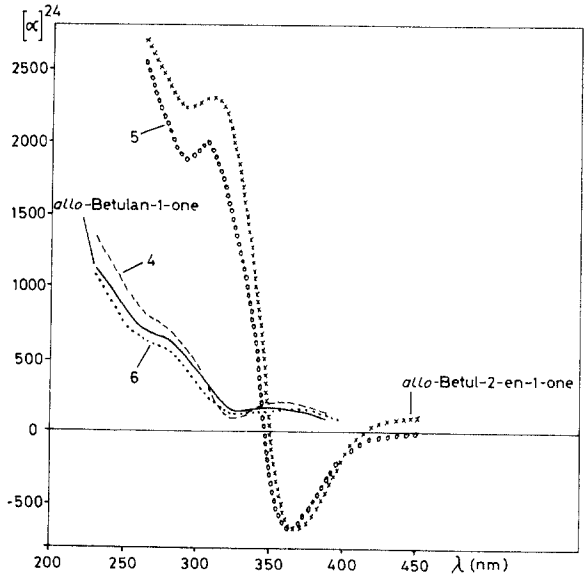


Fig. 1. ORD spectra of 3β-acetoxy-22-hydroxyhopan-1-one (**4**), 22-hydroxyhopan-1-one, 22-hydroxyhop-2-en-1-one (**5**), allo-betul-1-one and allo-betul-2-en-1-one.

^{1}H NMR spectrum of **2** (200 MHz, $CDCl_3$) showed, between δ4.5 and 4.7, two double doublets corresponding to the protons at C-1 and C-3, respectively. Irradiation at δ1.87 changed the double doublets into two doublets with $J_{a,a}$ = 13.0 Hz while irradiation at 1.66 changed the two double doublets into two doublets with $J_{a,e}$ = 5.0 Hz; hence, the multiplet at 1.87 corresponded to the equatorial H-2α and the multiplet at 1.66 to the axial H-2β. In the ketone, **4**, the axial H-2β (δ2.97, *t*, J_{gem} = 11.8 Hz) coupled with the equatorial H-2α (2.41, *dd*, $J_{a,e}$ = 5.0 Hz, J_{gem} = 11.8 Hz) and with the axial proton at C-3 (4.68, *dd*, $J_{a,e}$ = 5.0 Hz, $J_{a,a}$ = 11.8 Hz). The correlation of the signals was proved by double resonance experiments in the following way. Irradiation at δ2.41 transformed the triplet at 2.97 and the double doublet at 4.9 into a doublet with $J_{a,a}$ = 11.8 Hz; irradiation at 2.97 transformed the double doublet at 2.41 and the double doublet at 4.68 into doublets with $J_{a,e}$ = 5.0 Hz. Finally, irradiation at δ4.68 transformed the triplet at 2.97 and the double doublets at 2.41 into doublets with J_{gem} = 11.8 Hz, respectively. The ^{1}H NMR spectrum (100 MHz, $CDCl_3$) of the α,β-unsaturated ketone, **5**, showed two doublets at δ6.20 and 5.85 (J_{AX} = 10.0 Hz) corresponding to the vinylic protons at C-2 and C-3, respectively. These chemical shifts are in good agreement with the corresponding shifts of the vinylic protons of allo-betul-2-ene-1-one: H-2 at δ6.23 and H-3 at 5.63 (J_{AX} = 10.0 Hz). Contrary to this the doublets of the vinylic protons at C-3 and C-2 of allo-betul-1-en-3-one were situated at δ5.77 and 7.10 (J_{AX} = 10.0 Hz).

The signals of the ^{13}C NMR spectrum of **2** were correlated with C-12–C-22 and C-27–C-30 by their multiplicity and by comparison with the chemical shifts of 6-acetylzeorin and hopane [3]. Especially noteworthy are the singlets at δ73.9 in the ^{13}C NMR spectra of **2** and **6**, demonstrating the presence of the hydroxyisopropyl side chain. For the correlation of the ring A/B carbon atoms the influence of the acetoxy groups at C-1 and C-3 must be taken into consideration. The influence of the 3β-acetoxy group was derived from ^{13}C NMR data of lupane derivatives [3]. Because corresponding data of 1-acetoxylated hopanes or lupanes are unknown we estimated the influence of the acetoxy group in this position from data published for 1β-acetoxy-5α-androstanes [4]. The signals of C-23 and C-24 are shifted to higher field by reason of the γ-gauche effect between the 3β-acetoxy group and C-23 and C-24. The ^{13}C NMR chemical shifts and the multiplicity of the signals of **2** and **6** are summarized in Table 1.

The mass spectral fragmentation of the hopane derivatives **1**–**8** is mainly characterized by bond cleavages in ring C (Scheme 1) [2, 5]. Ions of type **b**, $[\mathbf{b}-H_2O]^+$ and $[\mathbf{b}-C_3H_6O]^+$ locate one hydroxyl group at C-22. The appearance of ions **d** and **e** is typical for hopanes with a 17(21)-double bond. The presence of two functional groups at ring A can be deduced from the mass spectral data of the keto derivatives **4** and **6**–**8**. The key ions **f** and **g** appear in analogy to 1-oxo-allo-betulanes [6]. The mass shifts of 2 a.m.u. towards lower masses in the mass spectra of **4** and **7** can be explained by an 1,2-elimination of the 3β-acetoxy function followed by ring-B cleavage leading to ions **f** and **g**.

3β-Acetoxy-1β,22-diol (**1**) is the first triterpene with an oxygen function at C-1 isolated from a lichen. It was also found recently in *Dirinaria aegialita* (Afz. in Ach.) Moore (Physciaceae) [Huneck, S., unpublished results].

Table 1. ^{13}C NMR chemical shifts (50.33 MHz, $CDCl_3$) and multiplicity (from SFORD-spectra) of the signals of 1β,3β-diacetoxyhopan-22-ol (**2**) and 1-oxohopan-22-ol (**6**)

C No.	2	6	C No.	2	6
1	80.3 *d*	217.4 *s*	16	21.9 *t*	22.0 *t*
2	30.0 *t*	35.5 *t*	17	53.9 *d*	54.1 *d*
3	76.4 *d*	43.0 *t*	18	43.9 *s*	44.2 *s*
4	37.8 *s*	33.3 *s*	19	41.2 *t*	41.3 *t*
5	52.8 *d*	57.4 *d*	20	26.6 *t*	26.6 *t*
6	17.7 *t*	19.3 *t*	21	51.1 *d*	51.2 *d*
7	32.9 *t*	32.7 *t*	22	73.9 *s*	73.9 *s*
8	42.3 *s*	42.3 *s*	23	27.8 *q*	32.0 *q*
9	50.7 *d*	41.5 *d*	24	16.9 *q*	22.6 *q*
10	42.2 *s*	52.4 *s*	25	12.8 *q*	29.7 *q*
11	23.0 *t*	23.8 *t*	26	16.0 *q*	15.1 *q*
12	24.0 *t*	24.1 *t*	27	16.9 *q*	17.1 *q*
13	49.3 *d*	50.5 *d*	28	16.1 *q*	16.2 *q*
14	41.9 *s*	41.9 *s*	29	28.7 *q*	28.7 *q*
15	34.5 *t*	34.5 *t*	30	30.9 *q*	30.8 *q*

Compound **2**: Me–CO–at 1β, 21.0 *q* and 170.0 *s*; Me–CO– at 3β, 21-7 *q* and 170.2 *s*.

EXPERIMENTAL

3β-Acetoxyhopan-1β,22-diol (**1**). *Pseudoparmelia texana* (Tuckerman) Hale (Venezuela, Estado Mèrida, El Pedregal de Jaji; leg. A. Morales Mendez, Feb. 1980, det. M. Lopez-Figueiras; voucher specimen under AMM No. 7 in the Herbarium of A. Morales Mendez) (200 g) was extracted with *n*-hexane, C_6H_6 and Me_2CO. The C_6H_6 and Me_2CO extracts were combined and recrystallized from $CHCl_3$–MeOH to yield **1** (3.5 g, 1.75%) in small plates of mp 273–275°. $C_{32}H_{54}O_4$. IR ν_{max}^{KBr} cm^{-1}: 834, 864, 892, 906, 916, 940, 962, 978, 1026, 1050, 1090, 1110, 1142, 1260, 1320, 1380, 1412, 1450, 1466, 1702, 2990, 3500, 3620. MS *m/z* (rel. int.): 502 $[M]^+$ (12), 484.3913 $[M-H_2O]^+$ (32) (calc. 484.3916), 466.3814 $[M-2H_2O]^+$ (7) (calc. 466.3811), 441.3377 $[M-H_2O-C_3H_7]^+$ (16) (calc. 441.3368), 424.3692 $[M-H_2O-HOAc]^+$ (20) (calc. 424.3700), 406 $[M-2H_2O-HOAc]^+$ (15), 384 $[M-C_3H_6O-HOAc]^+$ (17), 366.3291 $[M-H_2O-C_3H_6O-HOAc]^+$ (43) (calc. 366.3286), 355 (12), 351 (11), 305.2130 $[c]^+$ (12) (calc. 305.2117), 233 (10), 229 (17), 217 (32), 207 $[b]^+$ (73), 203 (49), 189.1653 $[b-H_2O]^+$ (100) (calc. 189.1653), 175 (56), 161 (58), 149 $[b-C_3H_6O]^+$ (98), 135 (58), 121 (50), 109 (44).

1β,3β-Diacetoxyhopan-22-ol (**2**). Compound **1** (0.1 g) in pyridine (6 ml) with Ac_2O (2 ml) was heated at 100° for 2 hr and chromatography of the crude acetate on Si gel (5 g) gave **2**. From $CHCl_3$–MeOH plates of mp 256–258° and $[\alpha]_D^{24}$ +37° ($CHCl_3$; *c* 0.86). $C_{34}H_{56}O_5$. IR ν_{max}^{KBr} cm^{-1}: 832, 862, 906, 920, 968, 990, 1030, 1116, 1140, 1162, 1240, 1370, 1450, 1468, 1720, 2990, 3580. ^1H NMR (200 MHz, $CDCl_3$): δ0.71 (3H, *s*, Me-28), 0.81 (6H, *s*, Me-23, Me-24), 0.90 (3H, *s*, Me-25), 0.93 (3H, *s*, Me-27), 0.98 (3H, *s*, Me-26), 1.15 (3H, *s*, Me-29), 1.17 (3H, *s*, Me-30), 1.66 (1H, *m*, H-2β), 1.87 (1H, *m*, H-2α), 1.95 (3H, *s*, OAc-1β), 1.99 (3H, *s*, OAc-3β), 4.57, (1H, *dd*, H-3α), 4.65 (1H, *dd*, H-1α). MS *m/z* (rel. int.): 544 $[M]^+$ (5), 526.4014 $[M-H_2O]^+$ (32) (calc. 526.4022), 484.3893 $[M-HOAc]^+$ (13) (calc. 484.3916), 483.3472 $[M-H_2O-C_3H_7]^+$ (17) (calc. 483. 3474), 466.3796 $[M-H_2O-HOAc]^+$ (26) (calc. 466.3811), 457 (24), 424.3692 $[M-2HOAc]^+$ (38) (calc. 424.3705), 406.3599 $[M-H_2O-2HOAc]^+$ (36) (calc. 406.3599), 391 (16), 366.3284 $[M-2HOAc-C_3H_6O]^+$ (66) (calc. 366.3286), 337 (20), 297 (14), 229 (20), 216 (35), 207 $[b]^+$ (34), 202 (63), 189.1645 $[b-H_2O]^+$ (100) (calc. 189.1643), 175 (53), 161 (56), 149 $[b-C_3H_6O]^+$ (77), 135 (56), 121 (54), 107 (48).

Hopan-1β,3β,22-triol (**3**). Compound **3** was prepared by saponification of **1** in EtOH (20 ml) with KOH (1 g) under reflux for 2 hr. After usual work-up and crystallization from $CHCl_3$–MeOH, flat needles of mp 246–248° and $[\alpha]_D^{24}$ +6° (pyridine; *c* 0.56). $C_{30}H_{52}O_3$. IR ν_{max}^{KBr} cm^{-1}: 832, 890, 910, 940, 1000, 1038, 1108, 1150, 1246, 1268, 1384, 1470, 3000, 3550. MS *m/z* (rel. int.): 460 $[M]^+$ (10), 442 $[M-H_2O]^+$ (17), 427 (10), 424 $[M-2H_2O]^+$ (13), 409 (7), 402 $[M-C_3H_6O]^+$ (12), 399 $[M-H_2O-C_3H_7]^+$ (16), 384 $[M-H_2O-C_3H_6O]^+$ (21), 373 (15), 263 $[c]^+$ (14), 245 $[c-H_2O]^+$ (9), 220 (29), 207 $[b]^+$ (57), 189 $[b-H_2O]^+$ (94), 175 (40), 161 (49), 149 $[b-C_3H_6O]^+$ (100), 135 (49), 121 (46), 109 (45).

1-Oxo-3β-acetoxyhopan-22-ol (**4**). To a soln of **1** (0.5 g) in pyridine (0.5 l.) was added CrO_3 (1 g) and the mixture kept at room temp. for 1 week. After usual work-up, chromatography on Si gel and crystallization from $CHCl_3$–MeOH gave needles (0.39 g) of mp 254–256° (dec.) and $[\alpha]_D^{24}$ +80° ($CHCl_3$; *c* 0.825). $C_{32}H_{52}O_4$. IR ν_{max}^{KBr} cm^{-1}: 846, 862, 898, 944, 970, 1030, 1076, 1108, 1136, 1160, 1250, 1380, 1460, 1702, 3000, 3640. ^1H NMR (200 MHz, $CDCl_3$): δ0.75 (3H, *s*, Me-28), 0.90 (3H, *s*, Me-24), 0.94 (3H, *s*, Me-27), 0.99 (3H, *s*, Me-26), 1.01 (3H, *s*, Me-23), 1.15 (3H, *s*, Me-29), 1.17 (3H, *s*, Me-30), 1.19 (3H, *s*, Me-25), 2.02 (3H, *s*, OAc-3β), 2.41 (1H, *dd*, H-2α), 2.97 (1H, *t*, H-2β), 4.68 (1H, *dd*, H-3α). MS *m/z* (rel. int.): 500.3874 $[M]^+$ (4) (calc. 500.3865), 482.3752 $[M-H_2O]^+$ (16) (calc. 482.3760), 467 (4), 439.3239 $[M-H_2O-C_3H_7]^+$ (10) (calc. 439.3212), 422.3546 $[M-H_2O-HOAc]^+$ (16) (calc. 422.3546), 413 (13), 407 (8), 379.3010 $[M-H_2O-C_3H_7-HOAc]^+$ (14) (calc. 379.3001), 353 (22), 311 (9), 243.1749 $[c-HOAc]^+$ (10) (calc. 243.1749), 233 (18), 217 (36), 203.1425 $[a-HOAc]^+$ (15) (calc. 203.1436), 189.1641 $[b-H_2O]^+$ (73) (calc. 189.1643), 175 (24), 161 (38), 150.1044 $[g]^+$ (100) (calc. 150.1045), 149 $[b-C_3H_6O]^+$ (39), 137 $[f]^+$ (49), 135 (57), 121 (62), 109 (58).

1-Oxohop-2-en-22-ol (**5**). Heating **4** (0.1 g) in MeOH (25 ml) and C_6H_6 (10 ml) with KOH (1.5 g) under reflux for 2.5 hr and usual work-up and crystallization from $CHCl_3$–MeOH gave needles of **5**, mp 246–250° and $[\alpha]_D^{24}$ +100° ($CHCl_3$; *c* 0.65).

$C_{30}H_{48}O_2$. IR ν_{max}^{KBr} cm^{-1}: 834, 942, 954, 976, 1008, 1038, 1068, 1130, 1144, 1170, 1190, 1236, 1270, 1326, 1370, 1460, 1660, 2970, 3550. ^1H NMR (100 MHz, $CDCl_3$): δ0.76 (3H, *s*, Me-28), 0.95 (3H, *s*, Me-23), 1.02 (3H, *s*, Me-24), 1.05 (6H, *s*, Me-26, Me-27), 1.14 (6H, *s*, Me-25, Me-29), 1.17 (3H, *s*, Me-30), 5.58 (1H, *d*, H-3), 6.20 (1H, *d*, H-2). MS *m/z* (rel. int.): 440 $[M]^+$ (2), 422 $[M - H_2O]^+$ (20), 407 (5), 382 $[M - C_3H_6O]^+$ (14), 367 (5), 353 (3), 243 $[\mathbf{c}]^+$ (4), 233 (52), 227 (20), 207 $[\mathbf{b}]^+$ (16), 203 $[\mathbf{a}]^+$ (15), 189 $[\mathbf{b} - H_2O]^+$ (67), 175 (21), 163 (24), 150 $[\mathbf{g}]^+$ (100), 149 $[\mathbf{b} - C_3H_6O]^+$ (66), 137 $[\mathbf{f}]^+$ (80), 122 (36), 107 (30).

1-*Oxohopan*-22-*ol* (**6**). Hydrogenation of **5** (0.1 g) in EtOH (50 ml) with Adams' catalyst (0.1 g) under normal conditions for 3 hr gave **6**. After usual work-up and crystallization from $CHCl_3$–MeOH, needles of mp 236–238° and $[\alpha]_D^{24}$ +84° ($CHCl_3$; *c* 0.685). $C_{30}H_{50}O_2$. IR ν_{max}^{KBr} cm^{-1}: 836, 860, 942, 982, 1010, 1044, 1138, 1370, 1390, 1450, 1464, 1684, 2980, 3550. ^1H NMR (200 MHz, $CDCl_3$): δ0.75 (3H, *s*, Me-28), 0.88 (3H, *s*, Me-24), 0.96 (3H, *s*, Me-23), 0.98 (3H, *s*, Me-26), 1.02 (3H, *s*, Me-27), 1.15 (3H, *s*, Me-29), 1.17 (3H, *s*, Me-30), 1.20 (3H, *s*, Me-25), 2.04 (1H, *m*, H-2α), 2.81, 2.88, 2.94 (1H, *ddd*, H-2β). MS *m/z* (rel. int.): 424 $[M - H_2O]^+$ (25), 409 (7), 381 $[M - H_2O - C_3H_7]^+$ (30), 355 (22), 313 (8), 245 $[\mathbf{c}]^+$ (27), 235 (47), 229 (32), 219 (43), 207 $[\mathbf{b}]^+$ (53), 205 $[\mathbf{a}]^+$ (37), 203 (44), 189 $[\mathbf{b} - H_2O]^+$ (100), 175 (67), 161 (80), 152 $[\mathbf{g}]^+$ (95), 149 $[\mathbf{b} - C_3H_6O]^+$ (94), 139 $[\mathbf{f}]^+$ (91), 135 (94), 121 (90), 109 (79).

3β-*Acetoxyhop*-17(21)-*en*-1-*one* (**7**). Compound **7** was obtained by treatment of **4** (10 mg) in HOAc (2 ml) with a soln of H_2SO_4 (0.3 ml) in HOAc (0.5 ml) at room temp. for 12 hr. After usual work-up and crystallization from $CHCl_3$–MeOH, plates of mp 270–271° (dec.). $C_{32}H_{50}O_3$. IR ν_{max}^{KBr} cm^{-1}: 830, 862, 920, 960, 968, 982, 1030, 1076, 1118, 1138, 1184, 1240, 1360, 1378, 1442, 1462, 1700, 1714, 2770. MS *m/z* (rel. int.): 482 $[M]^+$ (6), 467 (4), 439 $[M - C_3H_7]^+$ (8), 422 $[M - HOAc]^+$ (18), 407 (7), 379 $[M - HOAc - C_3H_7]^+$ (48), 243 $[\mathbf{c} - HOAc]^+$ (34), 217 (12), 203 $[\mathbf{a} - HOAc]^+$ (13), 189 $[\mathbf{b}]^+$ (32), 175 (33), 161 (52), 150 $[\mathbf{e}]^+$ and $[\mathbf{g}]^+$ (96), 137 $[\mathbf{f}]^+$ (96), 136 $[\mathbf{d}]^+$ (100), 135 (92), 121 (75), 107 (44).

Hop-17(21)-*en*-1-*one* (**8**). Treatment of **6** (20 mg) in HOAc (2 ml) with a soln of H_2SO_4 (0.3 ml) in HOAc (0.5 ml) at room temp. for 12 hr gave compound **8**. After usual work-up and crystallization from $CHCl_3$–MeOH, plates of mp 169–171° and $[\alpha]_D^{24}$ +88° ($CHCl_3$; *c* 1.585). $C_{30}H_{48}O$. IR ν_{max}^{KBr} cm^{-1}: 850, 954, 970, 1008, 1050, 1112, 1130, 1182, 1238, 1300, 1380, 1460, 1694, 2950. ^1H NMR (100 MHz, $CDCl_3$): δ0.87 (3H, *s*, Me), 0.89 (3H, *d*, Me-29), 0.93 (3H, *s*, Me), 0.94 (3H, *s*, Me), 0.94 (3H, *d*, Me-30), 1.04 (3H, *s*, Me), 1.07 (3H, *s*, Me-25). MS *m/z* (rel. int.): 424 $[M]^+$ (48), 409 (19), 381 $[M - C_3H_7]^+$ (82), 287 (9), 245 $[\mathbf{c}]^+$ (56), 219 (14), 205 $[\mathbf{a}]^+$ (15), 203 (36), 189 $[\mathbf{b}]^+$ (73), 177 (87), 161 (90), 152 $[\mathbf{g}]^+$ (86), 150 $[\mathbf{e}]^+$ (60), 149 (60), 139 $[\mathbf{f}]^+$ (83), 136 $[\mathbf{e}]^+$ (99), 135 (100), 121 (83), 111 (82).

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