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ACYCLIC DITERPENES FROM *PERYMENIUM HINTONII*†

EMMA MALDONADO,* MARISELA BELLO, JOSÉ LUIS VILLASEÑOR‡ and ALFREDO ORTEGA

Instituto de Química and ‡ Instituto de Biología, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán, 04510, D.F., México

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Key Word Index—*Perymenium hintonii*; Compositae; Heliantheae; phytanes; diterpenes; scopoletin; eridictyol-7-methyl ether; butein-4-methyl ether; friedeline; epifriedelanol.

Abstract—The aerial parts of *Perymenium hintonii* gave, in addition to known coumarins, flavonoids and triterpenes, two new phytane-type diterpenes named tuxpanolide and isotuxpanolide. Their structures were elucidated by 1D and 2D NMR techniques. © 1998 Elsevier Science Ltd. All rights reserved

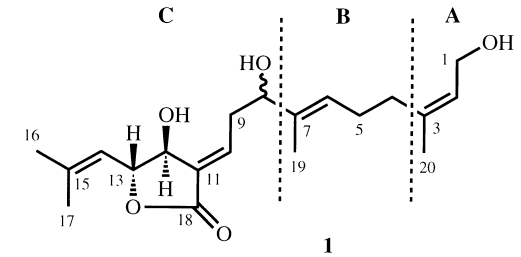
INTRODUCTION

As part of our systematic study on the genus *Perymenium* [1–3] we have examined the aerial parts of *P. hintonii* McVaugh (fam. Compositae tribe Heliantheae), a shrubby or treelike plant, up ca 4 m height, growing in Central México. In this species we have found phytane diterpenes, friedelanes, coumarins, chalcones and flavanones. These types of metabolites have not been described in any of the few investigated members of the genus [1–6].

RESULTS AND DISCUSSION

Perymenium hintonii afforded the known compounds sitosterol, scopoletin (7-hydroxy-6-methoxy coumarin) [7], friedelin (D:A-friedo-olean-3-one) [8, 9], epifriedelanol (D:A-friedo-oleanan-3β-ol) [8–10], ($\pm$)-eriodictyol-7-methyl ether (sternbine, ($\pm$)-5,3′,4′-trihydroxy-7-methoxy flavanone) [11–13] and butein-4-methyl ether (3,2′,4′-trihydroxy-4-methoxy chalcone) [14, 15]. The structures of these compounds were deduced from their spectroscopic data which were compared with those described in the literature. The correctness of the structures assigned to epifriedelanol and flavonoids were confirmed by preparation of their peracetyl derivatives. The unreported physical and spectroscopic data for these compounds are given in the experimental section.

The CI-mass spectrum of tuxpanolide (**1**) gave a peak at m/z 351 $[M+H]^+$ corresponding to the molecular formula $C_{20}H_{30}O_5$. The IR spectrum displayed absorption bands for hydroxyl (3354 cm^{-1}) and α,β-unsaturated-γ-lactone (1751, 1682 cm^{-1}). The ^1H, ^{13}C, COSY and HETCOR NMR spectra indicated that **1** was an acyclic diterpene constituted by the fragments A, B and C as evidentiated by the ^1H-^1H COSY spectrum in which three correlated spin systems were observed. In fragment A the vinyl proton at δ 5.19 (*tq*, $J = 7.5$, 1.5 Hz, H-2; δ 124.8 *d*, C-2) was coupled with a primary hydroxymethylene group (δ 3.79, 2H, *d*, $J = 7.5$ Hz, H-1; δ 58.9 *t*, C-1) and allylically, with a methyl group (δ 1.53, 3H, *br s*, H-20; δ 22.8 *q*, C-20). Fragment B showed a broad triplet for a vinylic proton at δ 5.26 ($J = 7$ Hz, H-6) which exhibited cross peaks with the partially overlapped multiplets of two methylenes at δ 1.94 (H-4) and 1.89 (H-5) and with the broad singlet of the vinylic methyl group at δ 1.40 (H-19). In the third fragment of compound **1** (C) an α,β-unsaturated-γ-lactone, a methylene, two trisubstituted double bonds, two secondary hydroxy and two vinylic methyl groups were present. The COSY



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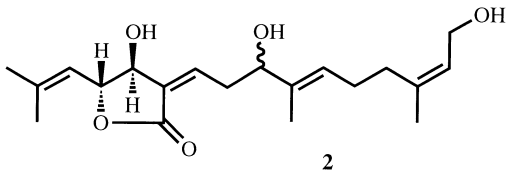

2

† Contribution No. 1653 of Instituto de Química, UNAM.
* Author to whom correspondence should be addressed.

Table 1. ^{1}H NMR data of compounds **1** and **2** (300 MHz, $CDCl_3$)

H	**1**	**1**†	**2**
1, 1′	4.04 *br d**	3.79 *d**	4.00 *br d**
	7.2	7.5	7
2	5.38 *tq*	5.19 *tq*	5.38 *br t*
	7.5, 1.5	7.5, 1.5	7.2
4	2.07 *br s*	1.94 *m*	2.11 *br s*
5	2.07 *br s*	1.89 *m*	2.11 *br s*
6	5.48 *br t*	5.26 *br t*	5.37 *br t*
	7	7	7
8	4.06 *dd**	3.80*	4.09 *br dd**
	10.5, 3		7.2, 3.9
9	2.54 *dt*	2.32 *dt*	2.71 *dt*
	13, 10.5	13, 10.6	13.5, 7.2
9′	2.42 *ddd*	2.10 *br ddd*	3.09 *ddd*
	13, 6.6, 3	13, 6.6, 3	13.5, 8, 3.9
10	6.92 *ddd*	6.81 *ddd*	6.10 *br t*
	10.5, 6.6, 1.8	10.6, 6.6, 1.8	~7.5
12	4.57 *br s*	4.38 *br s*	4.38 *br s*
13	5.06 *br s*	4.99 *dd*	4.83 *dd*
		9.3, 2	9, 4.2
14	5.06 *br s*	4.89 *d quint*	5.09 *br d*
		9.3, 1.2	9
16	1.79 *br s*	1.47 *br s*	1.72 *br s*
17	1.75 *br s*	1.52 *br s*	1.72 *br s*
19	1.63 *br s*	1.40 *br s*	1.57 *br s*
20	1.75 *br s*	1.53 *br s*	1.68 *br s*
OH	3.95 *br s*		3.95 *br s*

* Overlapped signals; † Determined in $CDCl_3$-C_6D_6.

spectrum showed that the signal at δ 3.80, ascribed to a proton geminal to an hydroxy group (H-8; δ 73.7 *d*, C-8), was coupled with the non-equivalent methylene protons at δ 2.32 and 2.10 (H-9, H-9′), which correlated with a vinyl proton at δ 6.81 (H-10). The chemical shift of this last proton is in accordance for a β-proton of an α,β-unsaturated-γ-lactone. This assumption was supported by the ^{13}C NMR signals at δ 142.0 *d* (C-10), 132.7 *s* (C-11) and 169.7 *s* (C-18). The proton at δ 6.81 correlated also with a broad singlet at δ 4.38 (H-12; δ 70.9 *d*, C-12) assigned to a proton attached to a carbon bearing a second hydroxy group. The last mentioned signal was coupled with a double doublet signal assigned to the proton under the lactone ring closure (δ 4.99, H-13; δ 82.7 *d*, C-13) which also correlated with a double quintuplet of an olefinic proton at δ 4.89 (H-14; δ 121.1, C-14). This, in turn, was coupled with the broad singlet signals of two vinylic methyls at δ 1.47 (H-16) and 1.52 (H-17).

The ^{1}H-^{13}C long-range couplings observed in the LR-HETCOR spectrum of tuxpanolide, confirmed the correctness of the partial structures A, B and C and led to the establishment of the gross structure of this compound as depicted in **1**. In addition, this experiment allowed the assignment of the ^{13}C singlet signals for carbons C-3, C-7, C-11, C-15 and C-18 which are shown in Table 2.

The NOESY spectrum showed the presence of NOEs (Fig. 1) between (i) H-1 and H-4 and (ii) H-2 and H-20 which established the configuration of the Δ^2-double bond as *Z*. The *E*-configuration of the Δ^6-double bond was supported by the NOE between H-6 and H-8 and by the chemical shift of the C-7 methyl group (δ 11.8 *q*) [16, 17]. The configuration of the Δ^{10}-double bond was established as *E* on the basis of the observed NOE between H-9 and H-12.

Although the absolute configuration at C-8, C-12 and C-13 was not determined, the magnitude of the $J_{12,13} = 2$ Hz was in agreement with a dihedral angle of ca 70 or 115° which requires a *trans*-relationship of H-12 and H-13. Thus, the structure of tuxpanolide was established to be the phytane-type diterpene **1** or its enantiomer.

The second diterpene isotuxpanolide (**2**) seemed to be a geometrical isomer of **1** as it was supported by the similarity of their IR, MS, 1D and 2D NMR spectra. The most significant differences observed in the ^{1}H NMR spectra of **1** and **2**, were the chemical shifts of the signals for H-9, H-9′ and H-10. In fact the C-9 protons of **2** were downfield (δ 2.71 and 3.09) from the corresponding signals in the spectrum of **1**, while the broad triplet signal for the olefinic H-10 was upfield (δ 6.10, $J = 7.5$ Hz) suggesting that **2** is the 10*Z*-isomer of **1**. This was confirmed by the observed NOE between H-10 and H-12. Other NOEs supporting structure **2** for isotuxpanolide are shown in Fig. 1.

EXPERIMENTAL

Plant material

Aerial parts of *Perymenium hintonii* McVaugh were collected 4.5 km south of Tuxpan, Michoacán in México, along the highway to Zitácuaro. A voucher specimen is deposited in the Herbarium of the Instituto de Biología, UNAM (MEXU-703747).

Extraction and isolation

Air-dried and powdered aerial parts of the plant (1.2 kg) were extracted successively with Me_2CO and MeOH at room temp. to give, after solvent evapn, 50.7 and 74.2 g of extracts, respectively. Both extracts were combined and submitted to partitioning between MeOH–H_2O (4:1) and hexane to give 91 g and 34.3 g of residues, respectively.

The hexane residue was decolourized with activated charcoal and chromatographed on a silica gel column eluted with a hexane–EtOAc gradient. Frs eluted with hexane afforded, after CC (silica gel, hexane) 6.5 mg of friedelin [8, 9] and 34.2 mg of epifriedelanol [8–10]. Sitosterol (2.37 g) was obtained from frs eluted with hexane–EtOAc (19:1).

The methanolic residue was chromatographed on a silica gel column (hexane–EtOAc gradient). Frs eluted with hexane–EtOAc (3:1) gave 23.1 mg of scopoletin

Table 2. ^{13}C NMR data (75 MHz, $CDCl_3$) and ^1H-^{13}C long-range couplings of compounds **1** and **2**

C mult*	**1**	**1**†	**2**	**1**†,‡	**2**‡
1*t*	58.9	58.3	58.7	H-2	
2*d*	124.7	124.8	124.7	H1, H20	H1, H20
3*s*	138.1	137.1	138.2	H4, H20	H1, H20
4*t*	31.1	30.8	31.0	H2, H20	H20
5*t*	24.9	24.7	24.8	H4, H6	
6*d*	125.8	125.3	124.7	H8, H19	H19
7*s*	137.4	137.1	136.7	H5, H8, H19	H5, H19
8*d*	73.9	73.7	75.5	H6, H9, H19	H19
9*t*	35.7	35.3	32.8	H8, H10	
10*d*	142.0	142.0	143.3	H8, H9, H12	
11*s*	133.3	132.7	130.9	H9, H10, H12, H13	
12*d*	71.1	70.9	75.0	H10, H13, H14	H10, H13
13*d*	82.9	82.7	81.9	H12, H17	H14
14*d*	121.0	121.1	120.7	H12, H13, H16, H17	H16
15*s*	140.1	139.4	141.2	H13, H16, H17	H16, H17
16*q*	25.7	25.1	25.7	H14, H17	H14, H15
17*q*	18.6	17.9	18.5	H14, H16	H14, H16
18*s*	170.0	169.7	169.1	H10, H12, H13	H10
19*q*	11.8	11.3	12.5	H6, H8	H6
20*q*	23.3	22.8	23.0	H2, H4	H4

* Multiplicity determined by DEPT experiments; † Determined in $CDCl_3$-C_6D_6; ‡ Long-range ^1H-^{13}C correlations in the LRHETCOR NMR spectra.

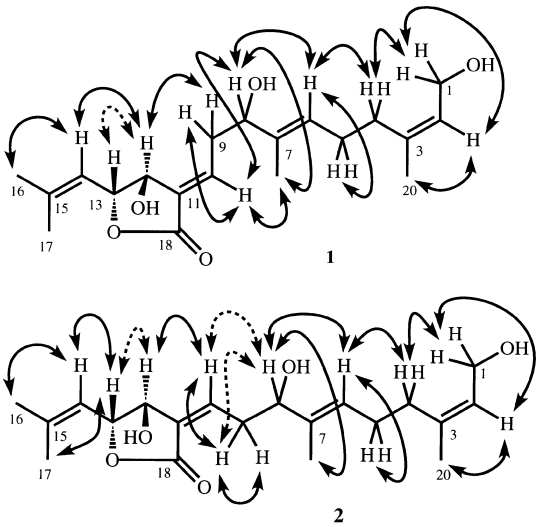

Fig. 1.NOEs of compounds **1** and **2** observed in the NOESY spectra.

[7]. Frs eluted with hexcane–EtOAc (7:3) afforded butein-4-methyl ether (128.1 mg) [14, 15] and eriodictyol-7-methyl ether (20.8 mg) [11–13]. Compound **1** (1.5 g) was eluted with hexane–EtOAc (3:2 and 1:1). It was purified by CC (silica gel, hexane–EtOAc 3:1) and percolation trough activated charcoal. Compound **2** (827.7 mg) was isolated from frs eluted with hexane–EtOAc (1:1 and 2:3) after treatment with activated charcoal and subsequent CC (silica gel, hexane–EtOAc 13:7).

Epifriedelanol (D:A-friedo-olean-3β-ol). Mp 292–294°; ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.8 (*t*, C-1), 35.3 (*t*, C-2)*, 72.7 (*d*, C-3), 49.2 (*d*, C-4), 37.8 (*s*, C-5), 41.7 (*t*, C-6), 17.5 (*t*, C-7), 53.2 (*d*, C-8), 37.1 (*s*, C-9), 61.4 (*d*, C-10), 35.5 (*t*, C-11), 30.6 (*t*, C-12), 39.7 (*s*, C-13), 38.4 (*s*, C-14), 32.3 (*t*, C-15), 36.1 (*t*, C-16), 30.0 (*s*, C-17), 42.8 (*d*, C-18), 35.2 (*t*, C-19), 28.2 (*s*, C-20), 32.8 (*t*, C-21), 39.3 (*t*, C-22), 11.6 (*q*, C-23), 16.3 (*q*, C-24), 18.2 (*q*, C-25), 20.1 (*q*, C-26), 18.6 (*q*, C-27), 32.1 (*q*, C-28), 31.8 (*q*, C-29), 35.0 (*q*, C-30). Acetylation of epifriedelanol, in the usual way, gave the acetyl derivative (mp, ^1H and ^{13}C NMR as reported in lit. [8–10]).

Butein-4-methyl ether (3,2′,4′-trihydroxy-4-methoxy chalcone). Mp 200–205°; ^1H NMR (300 MHz, $CDCl_3$-DMSO-d_6): δ 6.40 (*d*, $J = 2$ Hz, H-3′), 6.43 (*dd*, $J = 9$, 2 Hz, H-5′), 7.79 (*d*, $J = 9$ Hz, H-6′), 7.43 (*d*, $J = 15.3$ Hz, H-α), 7.74 (*d*, $J = 15.3$ Hz, H-β), 7.25 (*d*, $J = 2$ Hz, H-2), 6.88 (*d*, $J = 8.3$ Hz, H-5), 7.13 (*dd*, $J = 8.3$, 2 Hz, H-6), 3.92 (*s*, OMe), 13.45 (*s*, 2′-OH), 9.98 (*br s*, OH), 7.98 (*br s*, OH). ^{13}C NMR (75 MHz, $CDCl_3$-DMSO-d_6): δ 113.0 (*s*, C-1′), 165.9 (*s*, C-2′), 102.9 (*d*, C-3′), 164.6 (*s*, C-4′), 107.8 (*d*, C-5′), 131.2 (*d*, C-6′), 117.8 (*d*, C-α), 143.6 (*d*, C-β), 191.1 (*s*, CO), 127.6 (*s*, C-1), 113.7 (*d*, C-2), 146.2 (*s*, C-3), 149.5 (*s*, C-4), 110.8 (*d*, C-5), 121.6 (*d*, C-6), 55.5 (*q*, OMe). EIMS *m*/*z* (rel. int.): 286 $[C_{16}H_{14}O_5]^+$ (100), 285 (35), 269 (12), 257 (4), 243 (5), 177 (4), 163 (17), 150 (27), 137 (69), 109 (4). Acetylation of butein-4-methyl ether, in the usual manner, afforded the triacetyl derivative (3,2′,4′-triacetoxy-4-methoxy chalcone) as a pale yellow gum; ^1H NMR (300 MHz, $CDCl_3$): δ 7.00 (*d*, $J = 2$ Hz, H-3′), 7.11 (*dd*, $J = 8.4$,

2 Hz, H-5′), 7.70 (*d*, $J = 8.4$ Hz, H-6′), 7.01 (*d*, $J = 16$ Hz, H-α), 7.51 (*d*, $J = 16$ Hz, H-β), 7.30 (*d*, $J = 2.1$ Hz, H-2), 6.97 (*d*, $J = 8.4$ Hz, H-5), 7.41 (*dd*, $J = 8.4$, 2.1 Hz, H-6), 2.32, 2.31, 2.22 (3(3H, *s*, MeCO)), 3.87 (3H, *s*, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.8 (*s*, C-1′), 149.6 (*s*, C-2′), 117.0 (*d*, C-3′), 153.3 (*s*, C-4′), 119.1 (*d*, C-5′), 130.6 (*d*, C-6′), 123.8 (*d*, C-α), 144.3 (*d*, C-β), 190.2 (*s*, CO), 127.6 (*s*, C-1), 122.2 (*d*, C-2), 140.2 (*s*, C-3), 153.4 (*s*, C-4), 112.5 (*d*, C-5), 128.2 (*d*, C-6), 56.0 (*q*, OMe). EIMS *m*/*z* (rel. int.): 412 $[C_{22}H_{20}O_8]^+$ (37), 370 (57), 353 (4), 328 (79), 311 (12), 299 (8), 286 (59), 269 (13), 257 (13), 229 (9), 205 (4), 177 (7), 163 (13), 150 (22), 137 (100), 123 (6), 105 (7), 43 (44).

($\pm$)-Triacetyleriodictyol-7-methyl ether (($\pm$)-5,3′,4′-triacetoxy-7-methoxy flavanone). The title compound was obtained by acetylation of eriodictyol-7-methyl ether, in the usual way. Mp 157–162°; ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.44 (*dd*, $J = 13.2$, 3 Hz, H-2), 2.96 (*dd*, $J = 16.8$, 13.2 Hz, H-3_{ax}), 2.75 (*dd*, $J = 16.8$, 3 Hz, H-3_{eq}), 6.29 (*d*, $J = 2.5$ Hz, H-6), 6.43 (*d*, $J = 2.5$ Hz, H-8), 7.32 (*br s*, H-2′), 7.30 (*dd*, $J = 7$, 2.2 Hz, H-5′), 7.24 (*d*, $J = 7$ Hz, H-6′), 2.38, 2.30, 2.30 (3(3H, *s*, MeCO)), 3.83 (3H, *s*, OMe). ^{13}C NMR (75 MHz, $CDCl_3$): δ 78.5 (*d*, C-2), 45.0 (*t*, C-3), 188.2 (*s*, C-4), 151.9 (*s*, C-5), 105.0 (*d*, C-6), 165.6 (*s*, C-7), 99.6 (*d*, C-8), 163.9 (*s*, C-9), 108.0 (*s*, C-10), 137.3 (*s*, C-1′), 123.9 (*d*, C-2′), 142.4 (*s*, C-3′), 137.3 (*s*, C-4′), 124.1 (*d*, C-5′), 121.4 (*d*, C-6′), 55.8 (*q*, OMe), 21.1, 20.6, 20.6, (3(*q*, MeCO)), 169.4, 168.0, 168.0 (3(*s*, MeCO)). EIMS *m*/*z* (rel. int.): 428 $[C_{22}H_{20}O_9]^+$ (5), 413 (1), 386 (77), 344 (34), 302 (100), 301 (28), 193 (14), 167 (38), 136 (22), 123 (4), 110 (4), 95 (4), 78 (3), 43 (36).

Tuxpanolide (**1**). Pale yellow gum $[\alpha]_D$ −120.9° ($CHCl_3$, *c* 0.153); IR ($CHCl_3$) ν_{max} cm^{-1}: 3354, 1751, 1682, 1603, 1444, 1379, 1319, 1115, 1033, 1021, 972, 926, 868. CIMS *m*/*z* (rel. int.): 351 $[C_{20}H_{30}O_5+H]^+$ (4); EIMS *m*/*z* (rel. int.): 332 $[M-H_2O]^+$ (1), 315 [332–HO]$^+$ (2), 314 [332-H_2O]$^+$ (2), 297 [315-H_2O]$^+$ (3), 296 [314-H_2O]$^+$ (2), 248 [314-C_5H_6]$^+$ (6), 230 [296-C_5H_6]$^+$ (21), 215 [230-CH_3]$^+$ (8), 182 $[C_{11}H_{18}O_2]^+$ (60), 164 [182-H_2O]$^+$ (100), 149 [164-CH_3]$^+$ (37), 146 [164-H_2O]$^+$ (14), 139 $[C_9H_{15}O]^+$ (32), 135 [149-CH_2]$^+$ (32), 121 [135-CH_2]$^+$ (51), 107 [121-CH_2]$^+$ (23), 97 $[C_7H_{13}]^+$ (30), 93 [107-CH_2]$^+$ (61), 83 $[C_6H_{11}]^+$ (48), 69 $[C_5H_9]^+$ (33), 55 $[C_4H_7]^+$ (57), 41 $[C_3H_5]^+$ (56).

Isotuxpanolide (**2**). Pale yellow gum; $[\alpha]_D$ −188.5° ($CHCl_3$, *c* 0.160); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3406, 1750, 1676, 1603, 1447, 1380, 1122, 1033, 975, 925, 850. EIMS *m*/*z* (rel. int.): 332 $[M-H_2O]^+$ (2), 314 [332-H_2O]$^+$ (5), 296 [314-H_2O]$^+$ (8), 285 [314-CHO]$^+$ (6), 251 $[M-C_6H_{11}O]^+$ (7), 249 [314-C_5H_5]$^+$ (7), 230 [296-C_5H_6]$^+$ (17), 215 [230-CH_3]$^+$ (8), 182 $[C_{11}H_{18}O_2]^+$ (70), 164 [182-H_2O]$^+$ (100), 149 [164-CH_3]$^+$ (50), 146 [164-H_2O]$^+$ (20), 139 $[C_9H_{15}O]^+$ (48), 135 [149-CH_2]$^+$ (34), 121 [135-CH_2]$^+$ (73), 107 [121-CH_2]$^+$ (37), 93 [107-CH_2]$^+$ (88), 83 $[C_6H_{11}]^+$ (68), 69 $[C_5H_9]^+$ (56), 55 $[C_4H_7]^+$ (84), 41 $[C_3H_5]^+$ (93).

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