Phytochemistry, Vol. 27, No. 12, pp. 3897–3901, 1988.
Printed in Great Britain.

0031-9422/88 $3.00+0.00

AN ACYCLIC DITERPENE AND SESQUITERPENE LACTONES FROM *TITHONIA PEDUNCULATA*

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(*Received* 18 *March* 1988)

Key Word Index—*Tithonia pedunculata*; Heliantheae; flavonoids; heliangolides; eudesmanolides; germacrolide; acyclic diterpene.

Abstract—The aerial parts of *Tithonia pedunculata* afforded, in addition to several known compounds, three new substances: the heliangolide 15-hydroxy-3-dehydrotifruticin, the eudesmanolide 5α-hydroxytirotundifolin A and the acyclic diterpene (*E,E,E*)-3-hydroxymethyl-7,11-dimethyl-2,6,10-hexadecatrien-1,14,15-triol. Their structures were elucidated by spectroscopic methods and chemical transformations.

INTRODUCTION

The members of the genus *Tithonia* have a chemical composition [1], which resembles that of the genus *Viguiera* [2–4]. Plants of both genera (tribe Heliantheae) contain heliangolides and furoheliangolides as common constituents. Diterpenoids which are frequently present in *Viguiera* have not yet been reported from *Tithonia*. In the present study we describe two diterpenes (16-α-hydroxy-*ent*-kauran-19-oic acid and the new acyclic diterpene **6a**), two new sesquiterpene lactones (5α-hydroxytirotundifolin A, **1a** and 15-hydroxy-3-dehydrotifruticin, **3a**), and several known compounds.

DISCUSSION

The aerial parts of *T. pedunculata* Cronquist afforded the known compounds 16α-hydroxy-*ent*-kauran-19-oic acid [5], nevadensin [6], acerosin [7], eupatolide [8], the heliangolides leptocarpin [9] and 4 [10]. The eudesmanolides **1c**, **1e**, **1f** [11] were also found in this plant. In addition to the above mentioned known compounds, *T. pedunculata* yielded the new sesquiterpene lactones **1a** and **3a** as well as the acyclic diterpene **6a**.

5-Hydroxytirotundifolin A (**1a**) $C_{20}H_{26}O_7$, is an eudesmanolide with the same gross structure as tirotundifolin A (**1c**) [11]. The ^{1}H NMR spectra of both compounds showed a great similarity except for the downfield shift of H-1 and H-7 (Table 1), which indicates a close proximity with an α-oriented hydroxyl group attached to C-5 as evidenced by the inspection of Dreiding models. In order to confirm the relationship between the OH, H-1 and H-7, compounds **1a** and **1c** were oxidized affording respectively **1b** and **1d**. The dehydro compound **1b** which contains a 5α-hydroxy group shows its H-7 signal shifted abnormally to low field (δ3.63) as compared to that of H-7 in **1b** (δ2.76), which lacks the 5α-hydroxy group. Compound **1a** in a hot methanolic solution was partially transformed into a more polar compound, presumably **2a**. When the solvent was eliminated the remaining residue, after oxidation, afforded compounds **1b** and **2b**. A similar behaviour is reported for arbusculin C [12].

15-Hydroxy-3-dehydrotifruticin (**3a**), $C_{20}H_{24}O_8$, showed ^{1}H NMR spectroscopic data (Table 1) similar to those reported for 3-dehydrotifruticin (**3b**) [13]. The only difference between **3a** and **3b** is the presence in **3a** of a C-15 hydroxyl group. This was shown in the NMR spectrum by the absence of the low field methyl singlet of C-15, instead it appeared as a broad singlet at δ4.30 (2H) which on treatment with TAI was shifted downfield (AB system δ5.1 and 4.87, $J = 12$ Hz) due to the *in situ* esterification of the hydroxy group at C-15.

Compound **3a** was obtained by epoxidation of **4** [10], thus establishing the stereochemistry of **3a** as the same as that of **4** at C-6, C-7, C-8 and C-10. The stereochemistry of the epoxide should be as shown on the basis of the coupling constants ($J_{1,2} = 2$ Hz).

Compound **3a** upon catalytic hydrogenation afforded two crystalline substances, the hexahydro **5a** and the tetrahydro derivative **5b**, whose ester side chain has been isomerized.

The ^{13}C NMR spectrum of **3a** (Table 2) is in complete agreement with the proposed structure. Similarly, the ^{13}C NMR data of **4** obtained by APT experiments, are identical to those reported [10], with the only exception of the C-7 and C-9 signals, which are interchanged.

The acyclic diterpene **6a**, $C_{20}H_{36}O_4$, contains four hydroxy groups as shown spectroscopically. The IR spectrum exhibited bands at 3535 and 3443 cm^{-1}. The ^{13}C NMR spectrum (Table 2) showed two triplets at δ65.82 and 58.58, a doublet at 78.24, as well as a singlet at 73.15. This multiplicity indicated that two hydroxy groups are primary, one secondary and the last one is tertiary. This diterpene afforded, after mild acetylation, a 1:7 mixture of the diacetate **6b** and the triacetate **6c**. In compound **6b** only two primary hydroxy groups were acetylated and in triacetate **6c** the tertiary hydroxy group remains free. When **6c** was dehydrated, it yielded compound **7**, thus confirming the presence of the fourth hydroxy group. The position of the teritiary and second-

Table 1. ^{1}H NMR spectral data

H	1a*	1b	1d	2b	3a†	5a
1	4.12 *dd* (5, 11)				3.30 *d* (2)	3.17 *d* (2)
2					3.88 *d* (2)	3.54 *d* (2)
5					6.61 *br d* (5.6)	
6	4.7 *d* (11.5)	4.75 *d* (11.5)	4.6 *t* (11)	4.65 *d* (11.5)	5.82 *br d* (5.6)	4.8 *br d* (9)
7	3.8 *br ddd* (3, 6, 11.5)	3.63 *ddd* (3, 7, 11.5)	2.76 *m*	3.42 *br dd* (7, 11.5)	3.41 *br*	3.35 *m*
8	5.8 *br dd* (2, 6)	5.92 *br dd* (2.5, 7)	5.95 *br dd* (2, 6)	5.5 *br dd* (2.5, 7)	5.48 *m*	5.4 *m*
10						
13a	6.7 *d* (3)	6.13 *d* (3)	6.16 *d* (3)	6.45 *br*	6.32 *br d* (1)	1.08 *d* (7)
13b	5.4 *d* (3)	5.53 *d* (3)	5.5 *d* (3)	5.77 *br*	5.93 *br*	
14	1.05	1.35 5.32 *br d* (2)	1.35 5.25 *br*	1.30 5.22 *br*	1.23 4.30 *br*	1.1 3.88 *dd* (7.5, 10)
15	5.05 *br*	5.3 *br d* (2)	5.2 *br*	5.12 *br*		3.55 *dd* (5.5, 10)
16						
17						
18	3.0 *q* (5.5)	3.03 *q* (5.5)	3.02 *q* (6)	2.95 *q* (6)	6.12 *qq* (1.5, 7.3)	
19	1.26 *d* (5.5)	1.26 *d* (5.5)	1.25 *d* (6)	1.22 *d* (6)	1.95 *dq* (1.5, 7.3)	0.87 *t* (7)
20	1.52	1.5	1.5	1.5	1.5 *br*	1.07 *d* (7)
Others				3.76		

Run at 80 MHz, $CDCl_3$, TMS as int. standard. Values are in ppm.
Unmarked signals are singlets. Values in parentheses are coupling constants in Hz.
*In DMSO-d_6.
†Run at 200 MHz.

ary alcohol groups was established by treatment of **6a** with acetone, thus affording the acetonide **6d**. The manganese dioxide oxidation of this acetonide resulted in the dialdehyde **6e**, whose ^{1}H NMR spectrum showed the aldehydic protons with chemical shifts at δ9.5 and 10 which indicated a *trans*-relationship of the C-1 and the C-20 hydroxy group [14]. The geometry of the remaining double bonds was also established as *trans* by comparison of the chemical shifts of the ^{1}H NMR and ^{13}C NMR spectra of similar compounds [15, 16].

The chemical composition found for *T. pedunculata* is in agreement with its inclusion together with *T. fruticosa* in the series *Fruticosae* [17] and supports the accepted close relationship of this genus with *Viguiera*.

EXPERIMENTAL

Mps: uncorr. Chromatography was carried out over Kieselgel G. Known compounds were identified by direct comparison with authentic samples and spectroscopic data.

Plant material. Tithonia pedunculata Cronquist was collected in the State of Oaxaca, 5 km south of Portillo de Nejapan (voucher MEXU 398331, deposited in the Herbarium of the Instituto de Biología, UNAM).

Extraction and separation. Air-dried plant parts were extracted with hexane and EtOAc. The hexane extract (50 g) was chromatographed over silica gel eluting with hexane followed by hexane–EtOAc gradient. The EtOAc–hexane (4:1) fractions yielded 1.026 g of 16α-hydroxy-*ent*-kauran-19-oic acid. The EtOAc extract (110 g) was chromatographed using a hexane–EtOAc gradient elution system. After repeated CC on silica gel, the hexane–EtOAc (4:1) fractions afforded eupatolide (45.1 mg) and leptocarpin (330.2 mg). The hexane–EtOAc (7:3) fractions contained leptocarpin (1.746 g), tirotundifolin A (**1c**) (2.428 g), **1e** (2.28 g) and **1f** (474.7 mg). These compounds were analysed by HPLC using a micropack Si 10/25 cm column and eluted with $CHCl_3$–*i*-PrOH (24:1), flow rate 1 ml/min, speed chart 10 in/hr. The more polar part of these fractions was percolated using $CHCl_3$–hexane–Me_2CO (12:5:3), affording 5α-hydroxyrotundifolin A (**1a**) (30.2 mg). The hexane–EtOAc (3:2) fraction afforded 3.0 g of nevadensin. The hexane–EtOAc (2:3) fractions were combined and purified by repeated percolations with hexane–EtOAc (1:1) and $CHCl_3$–Me_2CO (1:1) yielding 9.114 g of **4**, 1.5 g of 15-hydroxy-3-dehydrotifruticin (**3a**), 1.2 g of

of compounds **1–3** and **5–7**

5b	6a	6b	6c	6d	6e	7
3.3 *d* (1.5)	4.16 *d* (7)	4.6 *d* (7.5)	4.6 *d* (7)	4.17 *d* (7)	10.17 *d* (8)	4.6 *d* (7.5)
3.48 *d* (1.5)	5.65 *t* (7)	5.6 *t* (7.5)	5.6 *t* (7.5)	5.65 *t* (7)	6.47 *d* (8)	5.6 *t* (7.5)
4.85 *br d* (8) 3.3 *m*	5.05 *m*	5.05 *m*	5.07 *m*	5.1 *m*	5.1 *m*	5.1 *m*
5.4 *m*						
	5.1 *m*	5.15 *m*	5.07 *m*	5.1 *m*	5.1 *m*	5.1 *m*
1.08 *d* (7)						
1.15 3.88 *dd* (3, 12) 3.7 *dd* (5, 12)	3.3 *dd* (3.5, 10)	3.32 *dd* (3.5, 10)	4.75 *dd* (5, 8)	3.63 *dd* (4, 8)	3.63 *dd* (4, 8)	5.06 *m*
	1.15 1.20	1.15 1.17	1.2 1.2	1.1 1.25	1.1 1.25	4.89 *m* 1.7 *br*
6.77 *br q* (7)	1.6 *br*	1.6 *br*	1.6 *br*	1.6	1.52 *br*	1.6 *br*
1.9 *br d* (7)	1.6 *br*	1.6 *br*	1.6 *br*	1.6	1.6 *br*	1.6 *br*
1.8 *br*	4.05 *br*	4.5 *br*	4.5 *br*	4.05 *br*	9.63	4.52 *br*
		2.05 2.07	2.05 2.07 2.1	1.33 1.43	1.33 1.42	2.06 2.1

acerosin and 4.5 g of (*E,E,E*)-3-hydroxymethyl-7,11-dimethyl-2,6,10-hexadecatrien-1,14,15-triol (**6a**).

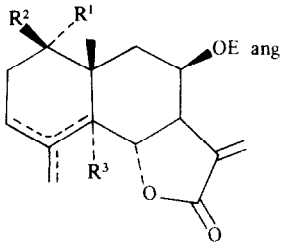
Compound **1a**. White crystals from MeOH, mp 276–279°. $[\alpha]_D = +58.9°$ (MeOH; *c* 0.190). UV λ_{max}^{MeOH} nm (ε): 209, (9421). IR ν_{max}^{Nujol} cm^{-1}: 3466, 3313, 1778, 1741. EIMS 70 eV, *m/z* (rel. int.): 378 $[M]^+$ (100), 262 $[M-RCO_2H]^+$ (4), 244 $[262-H_2O]^+$ (17), 226 $[262-2H_2O]^+$ (5), 83 $[C_5H_7O]^+$ (12), 71 $[C_4H_7O]^+$ (13), 55 $[C_4H_7]$ (18), 43 $[C_2H_3O]^+$ (98.9).

Compound **3a**. Pale yellow oil, $[\alpha]_D = 0.0$ ($CHCl_3$; *c* 0.202), UV λ_{max}^{MeOH} nm (ε): 210 (19427). 216 (21017). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3474, 1772, 1713, 1679, 1644. EIMS 70 eV, *m/z* (rel.int.): 292 $[M-RCO_2H]^+$ (1), 275 $[292-17]^+$ (4), 83 $[C_5H_7O]^+$ (100), 55 $[C_4H_7]^+$ (39.4), 43 $[C_2H_3O]^+$ (20.1): CD: $[\theta]_{204}$ 0.0, $[\theta]_{219}$ −48114, $[\theta]_{245}$ 0.0, $[\theta]_{258}$ + 13761, $[\theta]_{288}$ 0.0, $[\theta]_{337}$ − 2607 (MeOH; *c* 0.132).

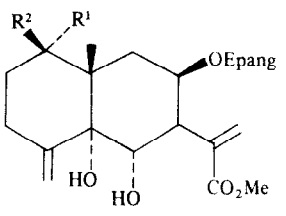
Compound **6a**. Colourless oil, $[\alpha]_{241} = +15.67°$ (MeOH; *c* 0.185), UV λ_{max}^{MeOH} nm (ε): 202 (14850). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3535, 3443, 1664, 1602. EIMS 70 eV, *m/z* (rel. int.): 289 $[M-2H_2O-15]^+$ (2), 229 $[M-C_5H_9O_2]^+$ (0.5), 153 $[C_{10}H_{17}O]^+$ (10), 135 $[C_{10}H_{15}]^+$ (12), 81 $[C_6H_9]^+$ (40.3), 71 $[C_4H_7O]^+$ (54.5), 59 $[C_3H_7O]^+$ (59.2), 55 $[C_4H_7]^+$ (40), 43 $[C_2H_3O]^+$ (100), 41 $[C_3H_5]^+$ (40).

Oxidation of **1a**. A soln of **1a** (23.5 mg previously heated in MeOH) in Me_2CO (10 ml), was treated with Jones reagent and worked-up in the usual manner. The mixture was chromatographed, eluting with $CHCl_3$ hexane–Me_2CO (6:2.5:1.5) yielding 4 mg of **1b** and 2.5 mg of **2b**. Compound **1b**: white crystals from hexane–Me_2CO, mp 204–206°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500, 1774, 1748, 1719. EIMS 70 eV, *m/z* (rel. int.): 376 $[M]^+$ (32.1), 260 $[M-RCO_2H]^+$ (13), 242 $[260-H_2O]^+$ (7), 71 $[C_4H_7O]^+$ (13), 55 $[C_4H_7]^+$ (22.9), 53 $[C_4H_5]^+$ (15), 43 $[C_2H_3O]^+$ (100). Compound **2b**: white crystals from hexane–Me_2CO mp 163–169°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3462, 1712, 1630. EIMS 70 eV, *m/z* (rel. int.): 408 $[M]^+$ (0.2), 390 $[M-H_2O]^+$ (0.3), 376 $[M-MeOH]^+$ (5.9), 292 $[M-RCO_2H]^+$ (61.4), 277 $[292-15]^+$ (23), 274 $[292-H_2O]^+$ (12.5), 260 $[292-MeOH]^+$ (11), 71 $[C_4H_7O]^+$ (15), 55 $[C_4H_7]^+$ (27), 53 $[C_4H_5]^+$ (15.5), 43 $[C_2H_3O]^+$ (100).

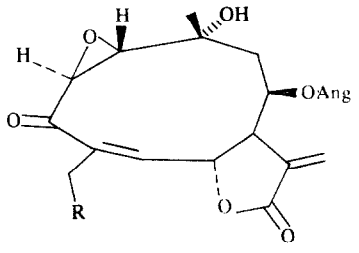
Oxidation of **1c**. A solution of **1c** (100 mg) in Me_2CO (10 ml) was oxidised with Jones reagent. The mixture was worked-up in the usual manner and chromatographed eluting with $CHCl_3$–hexane–Me_2CO (6:3:1) yielding 32.1 mg of **1c** and 52.5 mg of **1d** as white crystals from hexane–$CHCl_3$, mp 168–170°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1774, 1748, 1710, 1657. EIMS 70 eV, *m/z* (rel. int.): 360 $[M]^+$ (13.5), 345 $[M-15]^+$ (0.6), 332 [M



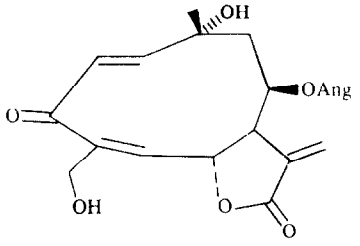
1a $\Delta^{4,15}$ R^1 = H, R^2 = R^3 = OH
1b $\Delta^{4,15}$ R^1 and R^2 = O, R^3 = OH
1c $\Delta^{4,15}$ R^1 = R^3 = H, R^2 = OH
1d $\Delta^{4,15}$ R^1 and R^2 = O, R^3 = H
1e $\Delta^{3,4}$ R^1 = R^3 = H, R^2 = OH
1f $\Delta^{4,5}$ R^1 = H, R^2 = OH



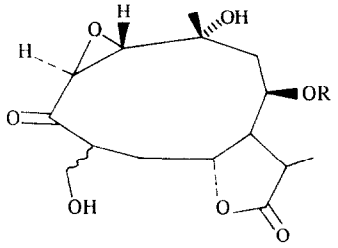
2a R^1 = H, R^2 = OH
2b R^1 and R^2 = O



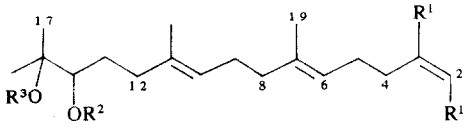
3a R = OH
3b R = H



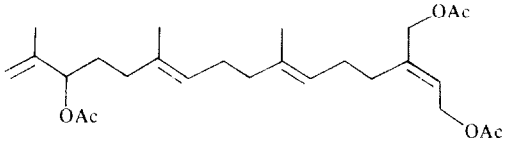
4



5a R = 2-MeBu
5b R = Tigl



6a R^1 = CH_2OH, R^2 = R^3 = H
6b R^1 = CH_2OAc, R^2 = R^3 = H
6c R^1 = CH_2OAc, R^2 = Ac, R^3 = H
6d R^1 = CH_2OH, R^2 and R = $C(Me)_2$
6e R^1 = CHO, R^2 and R^3 = $C(Me)_2$



7

$-28]^+$ (0.3), 244 $[M-RCO_2H]^+$ (23), 216 $[244-28]^+$ (5), 201 $[216-15]^+$ (16), 83 $[C_5H_7O]^+$ (12), 71 $[C_4H_7O]^+$ (12.5), 55 $[C_4H_7]^+$ (17.5), 53 $[C_4H_5]^+$ (12.5), 43 $[C_2H_3O]^+$ (100).

Epoxidation of **4**. To a soln of 58 mg of pure compound **4** in 5 ml $CHCl_3$, 370 mg of *m*-chloroperbenzoic acid were added and the mixture stirred at room temp. After 20 min the mixture was diluted with H_2O, extracted with $CHCl_3$, dried with Na_2SO_4 and concd. Chromatography of the crude product with hexane–EtOAc (11:9) afforded 7.7 mg of **3a**.

Hydrogenation of **3a**. A soln of compound **3a** (150 mg) in EtOAc (20 ml) was hydrogenated for 1 hr over 41 mg of 5% Pd-C at room temp. and atm. pres. The mixture was worked-up in the usual manner and purified by chromatography eluting with EtOAc–hexane (6:4) yielding 18.3 mg of **5a** and 39.8 mg of **5b**. Compound **5a**: white crystals from hexane–Me_2CO, mp 140–145°. IR ν_{max}^{Nujol} cm^{-1}: 3495, 3422, 1765, 1710. EIMS 70 EV, *m/z* (rel. int.): 380 $[M-H_2O]^+$ (0.5), 370 $[M-28]^+$ (0.4), 296 $[M-RCO_2H]^+$ (0.8), 278 $[296-H_2O]^+$ (1), 260 $[278-H_2O]^+$ (0.4), 85 $[C_5H_9O]^+$ (47.9), 57 $[C_4H_9]^+$ (100), 43 $[C_2H_3O]^+$ (37.3), 41 $[C_3H_5]^+$ (22.9). Compound **5b**: white crystals from hexane–Me_2CO, mp 224–228°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 1765, 1712, 1647. CIMS (CH_4) 200 eV, *m/z* (rel. int.): 396 $[M]^+$ (5), 378 [M

Table 2. ^{13}C NMR data of compounds **3a**, **4** and **6a**

C	3a	4(APT)	6a*
1	57.98 *d* (−)	161.99 *d* (−)	58.58 *t*
2	65.73 *d* (−)	129.69 *d* (−)	123.89 *d*
3	194.05 *s* (+)	196.36 *s* (+)	141.80 *s*
4	139.12 *s* (+)	135.81 *s* (+)	30.00 *t*
5	142.25 *d* (−)	137.11 *d* (−)	27.16 *t*
6	75.29 *d* (−)	75.76 *d* (−)	124.66 *d*
7	49.59 *d* (−)	46.90 *d* (−)	134.93 *s*
8	72.80 *d* (−)	73.94 *d* (−)	39.55 *t*
9	42.38 *t* (+)	48.43 *t* (+)	26.24 *t*
10	69.98 *s* (+)	71.89 *s* (+)	124.66 *d*
11	135.32 *s* (+)	141.62 *s* (+)	135.61 *s*
12	169.22 *s* (+)	169.79 *s* (+)	36.77 *t*
13	125.35 *t* (+)	124.95 *t* (+)	28.40 *t*
14	25.49 *q* (−)	28.55 *q* (−)	78.24 *d*
15	62.48 *t* (+)	62.64 *t* (+)	73.17 *s*
16	166.53 *s* (+)	166.42 *s* (+)	26.32 *q*[a]
17	126.55 *s* (+)	126.67 *s* (+)	23.49 *q*[a]
18	141.08 *d* (−)	140.35 *d* (−)	15.95 *q*[b]
19	20.04 *q* (−)	20.07 *q* (−)	16.06 *q*[b]
20	15.80 *q* (−)	15.71 *q* (−)	65.82 *t*

Run at 50 MHz, $CDCl_3$, $CDCl_3$ 77 Hz as int. standard (APT experiments)

*Run at 20 MHz, $CDCl_3$, TMS as int. standard.

[a,b]Assignments interchangeable.

$-H_2O]^+$ (25), 360 $[M-2H_2O]^+$ (7), 297 $[M+1-RCO_2H]^+$ (6), 279 $[297-H_2O]^+$ (3.5), 261 $[279-H_2O]^+$ (21), 111 (100).

Acetylation of **6a**. Compound **6a** (600 mg) was acetylated with 6 ml of pyridine and 6 ml of Ac_2O during 15 min at room temp. The mixture was worked-up in the usual manner and purified by percolation eluting with $CHCl_3$–Me_2CO (97:3) yielding 65 mg of **6b** and 444 mg of **6c**. Compound **6b**: Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3566, 1734, 1602. CIME (CH_4) 200 eV, *m/z* (rel. int.): 425 $[M+1]^+$ (13.7), 407 $[M+1-H_2O]^+$ (4.7), 347 $[407-HOAc]^+$ (6.8), 287 $[347-HOAc]^+$ (30), 269 $[287-H_2O]^+$ (12.5), 153 $[C_{10}H_{17}O]^+$ (50.5), 143 $[C_7H_{11}O_3]^+$ (100), 135 $[C_{10}H_{15}]^+$ (22), 127 $[C_7H_{11}O_2]^+$ (63.5). Compound **6c**: Colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450, 1732, 1602. CIME (CH_4) 200 eV, *m/z* (rel. int.): 467 $[M+1]^+$ (7.0), 449 $[M+1-H_2O]^+$ (100), 407 $[M+1-HOAc]^+$ (13), 389 $[407-H_2O]^+$ (44), 347 $[M+1-2HOAc]^+$ (52), 329 $[347-H_2O]^+$ (58.2), 287 $[M+1-3HOAC]^+$ (50), 269 $[287-H_2O]^+$ (63.5), 185 $[C_9H_{13}O_4]^+$ (27), 135 $[C_{10}H_{15}]^+$ (35), 127 $[C_7H_{11}O_2]^+$ (46.2), 125 $[C_7H_9O_2]^+$ (26).

Dehydration of **6c**. Compound **6c** (336 mg) in 4 ml pyridine was cooled to 0° and 1 ml $SOCl_2$ was added slowly. The mixture was poured into ice-water and extracted with $CHCl_3$. The organic layer was washed with 20% HCl aq. soln, $NaHCO_3$ satd, H_2O and dried with dry Na_2SO_4. The residue was percolated eluting with hexane–EtOAc (9:1) yielding 150.8 mg of **7** as colourless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1732, 1652, 1602. CIMS (CH_4) 200 eV, *m/z* (rel. int.): 449 $[M+1]^+$ (13), 389 $[M+1-HOAc]^+$ (11.5), 329 $[M+1-2HOAc]^+$ (27.5), 269 $[M+1-3HOAc]^+$ (100), 135 $[C_{10}H_{15}]^+$ (23.9).

Acetonide of **6a**. A soln of 350 mg of **6a** in 40 ml of dry Me_2CO and 6 g $CuSO_4$ (dry) was refluxed for 7 hr. The soln was filtered and concd under red. pres. The product was purified by chromatography with $CHCl_3$–Me_2CO (75:25) to yield 104 mg of **6d** as a colourless oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3360, 1660. EIMS 70 eV, *m/z* (rel. int.): 365 $[M-15]^+$ (8.5), 332 $[M-C_3H_6O]^+$ (0.3), 143 $[M-C_8H_{15}O_2]^+$ (9), 135 $[C_{10}H_{15}]^+$ (27), 81 $[C_5H_5O]^+$ (59.5), 71 $[C_4H_7O]^+$ (58.2), 67 $[C_5H_7]^+$ (25), 59 $[C_3H_7O]^+$ (41.1), 43 $[C_2H_3O]^+$ (100).

Oxidation of **6d**. Compound **6d** (40 mg) in 5 ml of $CHCl_3$ and 500 mg of MnO_2 were stirred at room temp. for 30 min. The mixture was filtered and purified by chromatography eluting with hexane–Me_2CO (9:1) to yield 20 mg of **6e** as an unstable colourless oily compound.

Acknowledgements—We are indebeted to R N Dr Miloš Budějínský CSc and R N Dr Soňa Vašicková from the Czechoslovak Academy of Science Institute of Organic Chemistry and Biochemistry for NMR and CD (**3a** and **4**) measurements, respectively. We also want to thank M.Sc. Jose Luis Villaseñor (Instituto de Biología, UNAM) for identification of the plant and to the chemists Lucía del Carmen Márquez, Jorge Cárdenas, Rubén Gaviño, René Villena, Misael Torres, Humberto Bojórquez and Luis Velasco for technical assistance.

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