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HYDROHALIMIC ACIDS FROM *HALIMIUM VISCOSUM*

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Key Word Index—*Halimium viscosum*; Cistaceae; diterpenoid acids; rearranged *ent*-labdanes; *ent*-halimanes.

Abstract—Several diterpenoid acids, with an *ent*-halimane skeleton, were isolated from the aerial parts of *Halimium viscosum* as methyl esters. Besides the well known hydrohalimic acid, acetoxyhydrohalimic acid, cinnamoyloxyhydrohalimic acid and 2-hydroxyhydrohalimic acid, three new ones have been identified as methyl 15-*Z*-cinnamoyloxy-1(10)-*ent*-halimen-18-oate, methyl 15-hydroxy-2-oxo-1(10)-*ent*-halimen-18-oate and methyl 15-methoxy-1(10)-*ent*-halimen-18-oate. Their structures have been determined by chemical and spectroscopic methods, using 2D correlation experiments (^1H–^{13}C and ^{13}C–^{13}C). Copyright © 1997 Elsevier Science Ltd

INTRODUCTION

A variety of diterpenoid structures and skeleta, many of them described for the first time, have been isolated during the last years from *Halimium viscosum* chemotypes in the Iberian peninsula and this has encouraged the search for another chemotype.

Villarino's *H. viscosum* contained only *ent*-halimane acids with a $\Delta^{1(10)}$ double bond, a carboxyl at C-4 as in the case of the major component halimic acid (**1**) [1, 2], and with polyfunctionalization [3] of the side chain or even its degradation [4]. Fregeneda's chemotype, however, contained only *ent*-halimane acids with a saturated side chain, e.g. hydrohalimic acid (**2**) [5, 6]. The neutral fraction of Fregeneda's *H. viscosum* contained a much greater variety of diterpenoid skeleta than the neutral part from Villarino's *H. viscosum* [7, 8]; in fact, 3-oxygenated labdanes [9, 10] such as 7,13*E*-labdadien-3β,15-diol (**3**), the major component, were isolated from it as well as other labdane alcohols. Moreover, four different carbon backbones were isolated from the extract: tormesane as in tormesol (**4**) [11, 12], tormesolane as in tormesolanone (**5**) [13], fregenedane as in fregenedadiol (**6**) [14–16] and isofregenedane as in isofregenedadiol (**7**) [17, 18]. Valparaíso's chemotype contained only labdane acids with a carboxyl group at C-17 such as zamoranic acid (**8**) [19, 20], with either a saturated or unsaturated side chain [20] and the neutral part afforded labdanes without an oxygenated function on ring A (e.g. **9**) [21] and tricyclic diterpenoid alcohols with valparane and valparolane skeleta such as valparene (**10**) [7, 22–24] and valparolone (**11**) [25], respectively.

In this work we have studied the composition of the acid part of *H. viscosum* (Celorico da Beira, Portugal) and isolated several diterpenoid acids, with a saturated side chain belonging to the *ent*-halimane class. Some of them are new and, for the well known acids, the spectroscopic assignment is completed with the ^{13}C NMR data.

RESULTS AND DISCUSSION

A hexane extract of *H. viscosum* (collected at Celorico da Beira, Portugal) was dewaxed with methanol and separated into neutral and acid parts. A small aliquot of the acid part was subjected to column chromatography on silica gel, and an acetoxy acid (**12**) (IR 2936, 1739, 1691 and 1241 cm^{-1}) and a hydroxy acid (**13**) (IR 3360 and 1691 cm^{-1}) were isolated. The ^1H NMR spectra of **1** and **2** were very similar: CH_2–$\underline{CH}$=C (δ 5.27, *br s*), four methyl groups, two of them doublets (δ 0.84 and 0.75; J = 5.0 and 7.0 Hz) and two singlets (δ 1.08 and 0.83), one of the latter (δ 1.08, *s*) being geminal to a carboxyl group. The main difference was observed in the CH_2–$\underline{CH_2}$–OAc group in **12** (δ 4.08, *m*) and the CH_2–$\underline{CH_2}$–OH group in **13** (δ ppm, 3.60, *m*). The ^{13}C NMR data for both compounds, except for the acetoxyl group signal in **12**, showed the same multiplicity for the 20 carbon atoms: i.e. four methyls, eight methylenes, one of them

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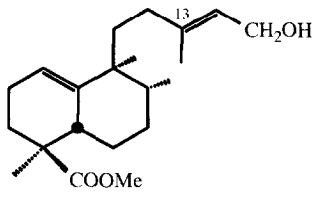
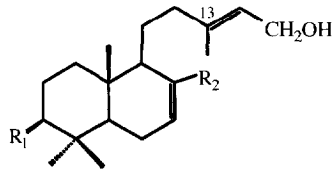
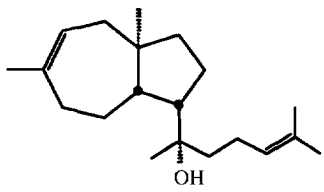




	R_1	R_2	
1			
2	13, 14-dihydro		
3	OH	Me	
8	H	COOMe	13, 14-dihydro



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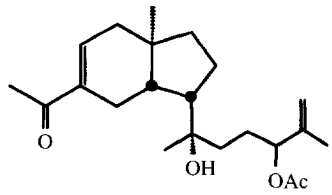

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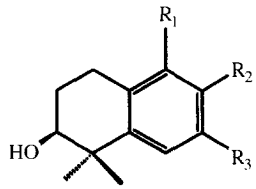
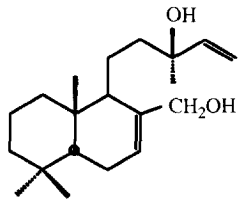


	R_1	R_2	R_3
6	$C_6H_{13}O$	Me	Me
7	Me	Me	$C_6H_{13}O$



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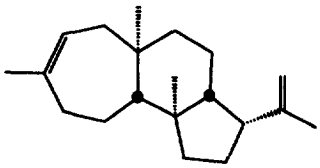

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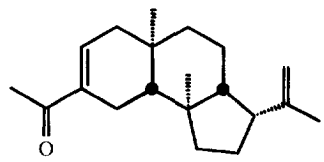

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directly bonded to an oxygen function (δ 63.2 and 60.9), four methines, one of them sp^2 hybridized (δ 119.5 and 119.3), and four fully substituted carbon atoms, one olefinic and one carboxyl.

When **12** and **13** were esterified with diazomethane, **14** and **15** were obtained, respectively, for which the spectroscopic data (Table 1) indicated the same similarities between **14** and **15** as for **12** and **13**. When **15** was acetylated **14** was obtained.

Two-dimensional heteronuclear experiments, XHCORR and COLOC, and a 2D homonuclear experiment, INADEQUATE, on **15** (Table 2) and comparison with an authentic sample (α_d + 67.6 specific rotation) allowed the identification of **13** as hydrohalimic acid and **12** as acetoxyhydrohalimic acid [5, 6]. Both compounds were described by us several years ago as methyl esters, isolated from *H. viscosum* (La Fregeneda) without ^{13}C NMR data [5].

The remainder of the acid part was esterifed with diazomethane and carefully chromatographed (column chromatography, silica gel_2) affording seven methyl esters (**14**–**20**). (The numbering is not in order of elution). Methyl esters **16**–**19** showed in their ^1H NMR spectra the same characteristics of the bian-

Table 1. ^{1}H NMR data for compounds **14–22** (250 MHz, $CDCl_3$)

H	**14**	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**
1	5.27, 1H, *t* (4.3)	5.16, 1H, *t* (4.3)	5.30, 1H, *t* (4.3)	5.31, 1H, *m*	5.32, 1H, *br s*	5.79, 1H, *s*	5.22, 1H, *br s*	5.79, 1H, *s*	5.87, 1H, *d* (5.9)
2							5.41, 1H, *dt* (4.4, 1.9)		4.69, 1H, *t* (4.9)
3						2.66, 1H, *d* (15.9) 2.24, 1H, *d* (15.9)		2.67, 1H, *d* (16.0) 2.25, 1H, *d* (16.0)	
5	2.63, 1H, *dd* (12.0, 3.8)	2.53, 1H, *dd* (12.0, 3.7)	2.65, 1H, *dd* (12.0, 3.4)	2.66, 1H, *m*	2.67, 1H, *m*	2.97, 1H, *dd* (12.8, 4.9)	2.71, 1H, *dd* (12.2, 3.6)	3.00, 1H, *dd* (12.5, 4.6)	2.20, 1H, *dd* (12.7, 4.9)
15	4.05, 2H, *m*	3.47, 2H, *m*	3.39, 2H, *t* (6.8)	4.14, 2H, *m*	4.23, 2H, *m*	3.63, 2H, *m*	4.07, 2H, *m*	4.06, 2H, *m*	4.04, 2H, *dt* (6.8, 2.0)
16	0.87, 3H, *d* (6.3)	0.83, 3H, *d* (6.5)	0.89, 3H, *d* (7.1)	0.88, 3H, *d* (6.5)	0.95, 3H, *d* (6.2)	0.88, 3H, *d* (6.1)	0.90, 3H, *d* (6.3)	0.90, 3H, *d* (6.3)	0.84, 3H, *d* (5.9)
17	0.75, 3H, *d* (7.0)	0.73, 3H, *d* (7.0)	0.78, 3H, *d* (6.9)	0.79, 3H, *d* (7.0)	0.79, 3H, *d* (7.0)	0.78, 3H, *d* (7.3)	0.81, 3H, *d* (7.0)	0.78, 3H, *d* (7.1)	0.77, 3H, *d* (7.8)
19	1.07, 3H, *s*	1.00, 3H, *s*	1.10, 3H, *s*	1.11, 3H, *s*	1.10, 3H, *s*	1.20, 3H, *s*	1.13, 3H, *s*	1.21, 3H, *s*	1.21, 3H, *s*
20	0.84, 3H, *s*	0.81, 3H, *s*	0.87, 3H, *s*	0.87, 3H, *s*	0.88, 3H, *s*	0.95, 3H, *s*	0.87, 3H, *s*	0.95, 3H, *s*	0.88, 3H, *s*
$CO_2\underline{CH_3}$	3.61, 3H, *s*	3.50, 3H, *s*	3.64, 3H, *s*	3.64, 3H, *s*	3.64, 3H, *s*	3.60, 3H, *s*	3.64, 3H, *s*	3.61, 3H, *s*	
2′				5.95, 1H, *d* (12.6)	6.43, 1H, *d* (16.0)				
3′				6.94, 1H, *d* (12.6)	7.67, 1H, *d* (16.0)				
5′,9′				7.57, 2H, *m*	7.51, 2H, *m*				
6′,7′,8′				7.33, 3H, *m*	7.37, 3H, *m*				
15-$O_2C\underline{CH_3}$ 2-$O_2C\underline{CH_3}$	2.00, 3H, *s*						2.02, 3H, *s* 2.04, 3H, *s*	2.02, 3H, *s*	2.02, 3H, *s*
$O\underline{CH_3}$			3.33, 3H, *s*						
OH		3.03, 1H, *br s*							

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

Table 2. NMR data for compound **15** and correlations observed in 2D experiment

Position	C	H	COLOC	INADEQUATE
1	119.0	5.16	2, 5, 9	2, 10
2	22.4	1.90		1
3	30.3	1.30–1.65	2, 18	4
4	44.5			3, 5, 18, 19
5	38.0	2.53	4, 10	4, 6, 10
6	22.6	1.10		5, 7
7	28.1	1.97	6, 17	6
8	38.1	1.40		7, 9, 17
9	42.4			8, 10, 11, 20
10	141.2			1, 5, 9
11	35.9	1.15–1.75	9, 12, 20	9, 12
12	30.6	0.92–1.00		11
13	29.7	1.30–1.60		14, 16
14	39.3	1.20–1.42		13, 15
15	60.5	3.47		14
16	19.5	0.83	12, 14	13
17	15.3	0.73	7, 9	8
18	178.4			4
19	19.7	1.00	3, 4, 5	4
20	22.2	0.81	8, 9, 10, 11	9
COOMe	51.4	3.50	18	

nular system described for **14** and **15**. The main difference resides in the function at C-15 (Table 3).

Compound **16** has a methoxyl group bonded to the methylene at C-15 (δ 3,39, *t*,J = 6.8 Hz, 71.23), **17** has a *Z*-cinnamoyloxy group –O–CO–CH=CH–C_6H_5 (δ 5.95, 6.94, *d*, J = 12.6 Hz, Table 1) while **18** has a *Z*-cinnamoyloxy group –O–CO–CH=CH–C_6H_5 (δ 6.43, 7.67, *d*, J = 16.0 Hz).

A small amount of **19** was separated from the most polar fraction of the Me esters together with a mixture from which **20** and **21** were isolated. Compound **20** is a methyl ester with similar characteristics to the previously isolated compounds with two acetoxyl groups: CH_2–CH_2–OAc and AcO–CH–CH=C (δ 4.07, *m*, and 5.41, *dt*, J_1 = 4.4 Hz and J_2 = 1.9 Hz). This secondary acetoxyl group can be positioned at C-2 in an *ent*-halimane skeleton. The multiplicity of the H-2 (*dt*) indicated an α-stereochemistry for the allylic group, which is confirmed later (see below).

Compound **19** has a –CO–CH=C– group with the carbonyl at C-2 conjugated with the annular double bond (δ 5.79, *s*). Acetylation of **19** gave **21** (UV λ_{max} = 241.0 nm). The 2-oxo structure for **19** was confirmed by treatment of compound **14** with Na_2CrO_4 to give **21** in good yield. Reduction of **21** with $NaBH_4$ gave **21**, and a mixture which after acetylation afforded **20**. However, reduction of **21** with aluminium isopropoxide afforded lactone **22** (16 mg).

EXPERIMENTAL

Spectral analysis. NMR: 250 or 400 MHz for ^1H and 62.9 or 100.1 MHz for ^{13}C. Chemical shifts are given in δ (ppm) and are referenced to the residual $CHCl_3$, 7.26 ppm for the ^1H and 77.0 ppm for ^{13}C, respectively. GC-MS: VG Trio 1000, 70 eV.

Extraction and isolation. Aerial parts of *H. viscosum* (131 g) collected in Celorico da Beira (Guarda, Portugal) were dried and extracted with *n*-hexane in a Soxhlet apparatus for 24 hr. The extract (10 g) was dewaxed with MeOH (0.8 g) and then extracted with 4% NaOH (6.4 g). The neutral fr. weighed 2.8 g. An aliquot (500 mg) of the acid part was subjected to CC on silica gel, affording **12** (10 mg) and **13** (200 mg). The remaining acid part (5.9 g) was esterified with CH_2N_2 and then the Me esters were subjected to CC on silica gel with *n*-hexane–EtOAc mixts giving three frs (I–III).

CC of fr. I on silica gel/10% $AgNO_3$ gave **16** (18 mg), **18** (9 mg) and **14** (25 mg). CC of fr. II on silica gel gave **15** (2.05 g). CC of fr. III on silica gel gave **19** (17 mg). Acetylation of a part of fr. III followed by CC on silica gel afforded **20** (18 mg) and **21** (39 mg).

Acetoxyhydrohalimic acid (**12**). Oil. IR ν_{max}^{film} cm^{-1}: 2936, 2869, 1739, 1691, 1463, 1375, 1241; ^1H NMR: δ 5.32 (1H, *dt*, J = 5.0, 2.5 Hz, H-1), 4.08 (2H, *m*, H-15), 2.65 (1H, *dd*, J = 12.5, 2.5 Hz, H-5), 2.04 (3H, *s*, O_2CCH_3), 1.14 (3H, *s*, Me-19), 0.89 (3H, *d*, J = 4.8 Hz, Me-16), 0.88 (3H, *s*, Me-20), 0.80 (3H, *d*, J = 7.0 Hz, Me-17); ^{13}C NMR: Table 3.

Hydrohalimic acid (**13**). Oil. IR ν_{max}^{film} cm^{-1}: 3360, 2910, 1691, 1456, 1369, 1281; ^1H NMR: δ 6.93 (1H, *br*, CO_2H), 5.27 (1H, *br*, H-1), 3.60 (2H, *m*, H-15), 2.61 (1H, *d*, J = 9.8 Hz, H-5), 1.08 (3H, *s*, Me-19), 0.84 (3H, *d*, J = 5.0 Hz, Me-16) 0.83 (3H, *s* Me-20), 0.75 (3H, *d*, J = 6.7 Hz, Me-17); ^{13}C NMR: Table 3.

Methyl 15-acetoxy-1(10)-ent-halimen-18-oate (**14**). Oil. IR ν_{max}^{film} cm^{-1}: 3057, 1736, 1461, 1378, 1243, 1166;

Table 3. ^{13}C NMR data of compounds **12**–**22** (62.9 MHz, $CDCl_3$)

C	12	13	14	15	16	17	18	19	20	21	22
1	119.5	119.3	119.3	119.0	119.2	119.4	119.4	124.8	119.9	124.8	122.8
2	22.7	22.7	22.7	22.4	22.7	22.8	22.7	197.2	69.1	197.1	72.2
3	30.2	30.1	30.6	30.3	30.8	30.8	30.8	43.0	33.5	43.1	37.4
4	44.6	44.6	44.8	44.5	44.8	44.9	44.9	46.2	44.7	46.2	44.7
5	38.1	38.0	38.2	38.0	38.2	38.3	38.3	40.5	38.2	40.5	41.2
6	23.0	23.0	22.8	22.6	22.8	22.9	22.9	23.4	23.7	23.4	22.3
7	28.4	28.4	28.3	28.1	28.3	28.4	28.4	28.2	28.8	28.2	28.1
8	38.6	38.5	38.3	38.1	38.3	38.4	38.4	41.0	39.4	41.0	38.8
9	42.9	42.7	42.7	42.4	42.7	42.8	42.8	45.2	43.4	45.2	42.6
10	141.4	147.5	141.4	141.2	141.5	141.5	141.5	169.9	147.0	169.7	149.6
11	35.4	35.8	35.4	36.0	36.6	35.4	35.6	36.4	35.3	35.2	35.3
12	30.8	30.5	30.8	30.6	31.0	30.9	30.9	30.9	30.8	31.0	30.7
13	30.5	29.8	30.5	29.8	30.4	30.5	30.6	30.2	30.6	30.5	30.2
14	36.6	39.1	36.5	39.3	36.6	36.5	36.6	39.4	36.2	36.6	35.5
15	63.2	60.9	63.1	60.5	71.2	63.1	63.3	60.9	63.1	62.9	63.0
16	19.6	19.7	19.6	19.5	19.9	19.6	19.8	19.6	19.6	19.5	19.1
17	15.6	15.5	15.5	15.3	15.6	15.6	15.6	15.5	15.5	15.5	15.3
18	184.7	184.1	178.5	178.4	178.6	178.6	178.6	176.8	177.3	176.7	181.9
19	20.2	20.3	19.9	19.7	19.9	19.9	19.9	21.2	21.9	21.1	19.5
20	22.4	22.3	22.5	22.2	22.6	22.6	22.6	21.9	23.6	21.9	21.8
$COOCH_3$			51.6	51.4	51.7	51.7	51.7	52.4	52.0	52.4	
1′						166.3	167.1				
2′						142.9	144.5				
3′						120.0	118.3				
4′						135.0	134.5				
5′						128.0	128.0				
6′						129.6	128.8				
7′						128.9	130.2				
8′						129.6	128.8				
9′						128.0	128.0				
OCH_3					58.6						
15-OOCMe	171.3		171.1						171.2	171.1	171.2
15-OOCCH_3	21.0		21.0						21.0	21.0	21.0
2-OOCMe									170.8		
2-OOCCH_3									21.5		

^1H and ^{13}C NMR: Tables 1 and 3; GC-MS 70 eV, *m/z* (rel. int.): 378 $[M]^+$ (1), 236 (16), 235 (97), 176 (26), 175 (100), 147 (12), 133 (15), 119 (28), 107 (13), 105 (38), 95 (12), 93 (16), 91 (20), 81 (15), 69 (17), 55 (43).

Methyl 15-*hydroxy*-1(10)-ent-*halimen*-18-*oate* (**15**). Oil; $[\alpha]_D^{22} = +67.65$ ($CHCl_3$, *c* 2.365); IR ν_{max}^{film} cm^{-1}: 3364, 3044, 1731, 1380, 1164, 1054; ^1H and ^{13}C NMR: Tables 1–3; GC-MS 70 eV, *m/z* (rel, int.): 336 $[M]^+$ (<1), 236 (11), 235 (75), 175 (100), 133 (10), 119 (19), 105 (25), 93 (10), 91 (16), 69 (19), 55 (52).

Methyl 15-*methoxy*-1(10)-ent-*halimen*-18-*oate* (**16**). Oil. IR ν_{max}^{film} cm^{-1}: 2930, 1725, 1462, 1375, 1248, 1187; ^1H and ^{1}C NMR: Tables 1 and 3; GC-MS 70 eV, *m/z* (rel. int.): 350 $[M]^+$ (≪1), 236 (15), 235 (100), 176 (16), 175 (95), 119 (14), 105 (16).

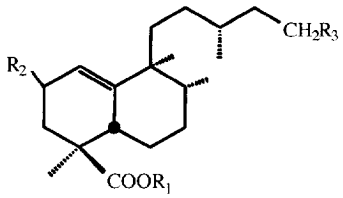
Methyl 15-*Z-cinnamoyloxy*-1(10)-ent-*halimen*-18-*oate* (**17**). Oil. IR ν_{max}^{film} cm^{-1}: 2922, 1731, 1712, 1631, 1470, 1389, 1254, 1153, 830, 763, 689; ^1H and ^{13}C NMR: Tables 1 and 3; GC-MS 70 eV, *m/z* (rel. int.): 466 $[M]^+$ (2), 263 (17), 235 (100), 207 (18), 175 (61), 147 (14), 131 (40), 103 (17).

Methyl 15-*cinnamoyloxy*-1(10)-ent-*halimen*-18-*oate* (**18**). Oil. IR ν_{max}^{film} cm^{-1}: 3064, 1726, 1705, 1664, 1380, 1166, 981, 765, 709; ^1H and ^{13}C NMR: Tables 1 and 3; GC-MS 70 eV, *m/z* (rel. int.): 466 $[M]^+$ (2), 236 (16), 235 (100), 207 (28), 175 (51), 131 (43), 103 (19), 77 (10).

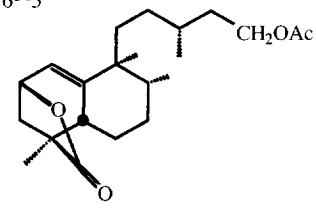
Methyl 15-*hydroxy*-2-*oxo*-1(10)-ent-*halimen*-18-*oate* (**19**). Oil. IR ν_{max}^{film} cm^{-1}: 3384, 3064, 1728, 1664, 1611, 1380, 1157, 823; ^1H and ^{13}C NMR: Tables 1 and 3; GC-Ms 70 eV, *m/z* (rel. int.): 350 $[M]^+$ (5), 189 (26), 161 (17), 147 (11), 122 (10), 121 (100), 55 (17).

Methyl 2,15-*diacetoxy*-1(10)-ent-*halimen*-18-*oate* (**20**). Oil. IR ν_{max}^{film} cm^{-1}: 3060, 1757, 1717, 1650, 1380, 1245, 1156; ^1H and ^{13}C NMR: Tables 1 and 3; GC-Ms 70 eV, *m/z* (rel. int.): 436 $[M]^+$ (≪1), 174 (15), 173 (100), 159 (15), 145 (35), 131 (31), 119 (19), 105 (62), 55 (21).

Methyl 15-*acetoxy*-2-*oxo*-1(10)-ent-*halimen*-18-*oate* (**21**). Oil. IR ν_{max}^{film} cm^{-1}: 3057, 1734, 1675, 1610, 1380, 1240, 1160; UV λ_{max} = 241.0 nm (ε = 13 000); ^1H and ^{13}C NMR: Tables 1 and 3; GC-MS 70 eV, *m/z* (rel. int.): 392 $[M]^+$ (4), 189 (37), 175 (10), 161 (22), 147 (12), 135 (10), 121 (100), 105 (10), 91 (10), 55 (19).



	R_1	R_2	R_3
12	H	H	OAc
13	H	H	OH
14	Me	H	OAc
15	Me	H	OH
16	Me	H	OMe
17	Me	H	$OCOCH \overset{Z}{=} CHC_6H_5$
18	Me	H	$OCOCH \overset{E}{=} CHC_6H_5$
19	Me	=O	OH
20	Me	OAc	OAc
21	Me	=O	OAc



22

Acetylation of fraction III. A portion of fr. III (62 mg) was treated with 1 ml Ac_2O and pyridine. The acetylated product (71 mg) was recovered and subjected to CC on silica gel, affording **20** and **21** (39 mg).

Allylic oxidation of **14** *with* Na_2CrO_4. To **14** (117 mg) in C_6H_6 (0.5 ml) were added dry NaOAc (85 mg), Ac_2O (0.7 ml) and HOAc (0.4 ml) and heated to 40°. When the reaction was complete, H_2O was added and after 1 hr the mixt. was extracted with Et_2O. The ethereal part was washed with $KHCO_3$ and H_2O to give 145 mg crude product. Silica gel CC, eluting with *n*-hexane–EtOAc (4:1), yielded **21** (87 mg, 74% yield).

Reduction of **21** *with* $NaBH_4$. To a soln of **21** (87 mg) in MeOH (10 ml), $NaBH_4$ (3.5 mg) was added. The mixt. was kept at room temp. for 7 hr, then H_2O and a few drops of 2M HCl were added. The mixt. was extracted with Et_2O and washed with H_2O. Evapn of the solvent gave a crude product (78 mg). CC on silica gel afforded **22** (3 mg, *n*-hexane–EtOAc, 9:1) and a mixt. (37.0 mg), which was acetylated following the usual procedure. The acetylated product (46.0 mg) was recovered and subjected to CC on silica gel, affording **20** (13.0 mg, 28%) and **21** (22.0 mg, 48%).

Reduction of **21** *with aluminum isopropoxide*. To a soln of **21** (67 mg) in *iso*-PrOH (3 ml) Al isopropoxide (140 mg) was added. The mixt. was kept at 56° for 7 hr, was then extracted with Et_2O after adding H_2O. The Et_2O phase was washed with 0.5 M HCl, 10% NaOH and H_2O, dried and evapd to give 57 mg of a mixt. which, on silica gel CC, yielded **22** (16 mg).

15-*Acetoxy*-1(10)-ent-*halimen*-18,2*β*-*olide* (**22**). Oil. IR ν_{max}^{film} cm^{-1}: 2949, 1795, 1732, 1631, 1456, 1368, 1241; ^1H and ^{13}C NMR: Tables 1 and 3; GC-MS 70 eV, *m/z* (rel. int.): 392 $[M]^+$ (≪1), 334 (16), 292 (2), 207 (17), 191 (56), 189 (15), 175 (12), 173 (22), 164 (14), 163 (67), 161 (18), 152 (11), 151 (14), 149 (13), 147 (13), 137 (14), 135 (48), 133 (12), 123 (22), 122 (21), 121 (24), 119 (15), 109 (41), 108 (79), 107 (37), 95 (78), 93 (41), 91 (30), 83 (33), 81 (78), 79 (52), 77 (25), 69 (58), 67 (42), 55 (100), 45 (23).

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