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SESQUITERPENE LACTONES AND A SECO-CARYOPHYLLENE DERIVATIVE FROM *MONTANOA KARWINSKII*

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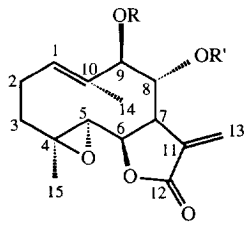
Key Word Index—*Montanoa karwinskii*; Asteraceae; Heliantheae; sesquiterpene lactones; germacrolides; seco-caryophyllene derivative.

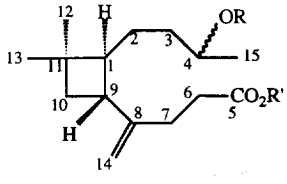
Abstract—Leaves of *Montanoa karwinskii* afforded in addition to known sterols, triterpenes and kaurane derivatives, four germacra-12,6β-olides. Three were new compounds, karwinsinolides A, B and C. Their structures were established by spectral methods, mainly NMR. A new seco-caryophyllene derivative was also isolated.

INTRODUCTION

Montanoa karwinskii A.P. de Candolle is most closely related to *M. atriplicifolia* and *M. pteropoda* and placed by V. Funk in the series Hibiscifoliae, together with *M. hibisciofolia*, *M. hexagona* and *M. leucantha* [1]. In continuation of our studies on the chemistry of *Montanoa* species, we have analysed the herbaceous parts of *M. karwinskii*, which resulted in the isolation of 12,6-*cis*-lactonized germacrolides which seem to be characteristic of the genus. In addition, a new seco-caryophyllene derivative was isolated as well as common terpenoids. We now report the structures of the new lactones which we named karwinsinolides A (**1**), B (**2**) and C (**3**) and the new acid 4-hydroxy-4,5-seco-caryophyllen-5-oic acid (**6**). Their structures and stereochemistry were established by spectroscopic methods, mainly ^{1}H NMR. The molecular structure of karwinsinolide A (**1**), was confirmed by single crystal X-ray diffraction.



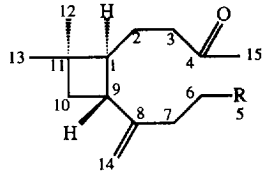
	R	R'
1)	Ac	Ang
2)	Ang	H
3)	H	Ang
4)	Ang	Ac
5)	Sen	H



6) R= R'= H

7) R= H, R'= Me

8) R= Ac, R'= H



9) R= COOMe

10) R= CH_2-OH

RESULTS AND DISCUSSION

The petrol and dichloromethane extracts of the leaves of *Montanoa karwinskii* afforded caryophyllene oxide, β-carotene, the ubiquitous sitosterol and stigmasterol; common pentacyclic triterpenes β-amirin, taraxasterol, taraxasteryl acetate and tarasteryl fatty esters (mainly palmitate); the kaurane diterpenes ent-kaurenic acid, angeloyl and senecioyl grandifloric acids. In addition, four 12,6β-germacrolides were obtained, the known 9β-senecioyloxy-4β,5α-epoxy-*trans*-germacra-1(10)-en-12,6β-olide (**5**), previously isolated from *M. mollisima* [2], and three new closely related ones, karwinsinolides A (**1**), B (**2**) and C (**3**). A new sesquiterpenic acid characterized as 4-hydroxy-4,5-seco-caryophyllen-5-oic acid (**6**) was also isolated. This is the third compound of this type isolated from a natural source.

Karwinsinolide A (**1**), $C_{22}H_{28}O_7$ (CIMS: $[M + 1]^+$ at *m/z* 405), was isolated as a crystalline compound, mp 204–206°, and characterized as an α,β-unsaturated γ-lactone containing a saturated ester and an α,β-unsaturated one (IR absorption bands at 1777, 1737 and 1720 cm^{-1}). The ester substituents were assigned to an acetate and an angelate group based on the typical ^{1}H NMR signals (Table 1), together with the characteristic mass spectral peaks at *m/z* 43 for the acetate and 83 and 55 for the angelate moieties. Other peaks at *m/z* 344

Contribution No. 1256 of Instituto de Química, UNAM.

Table 1. ^{1}H NMR spectral data for **1–4** (200 MHz, TMS as int.standard)

	1		2		3		4
H	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$	C_6D_6	$CDCl_3$
1	5.75 *br d*	5.21	5.60 *br d*	5.57	5.82 *br d*	5.20	5.68 *obs*
5	3.16 *br d*	2.96	3.00 *br d*	3.06	3.19 *br d*	2.94	3.14 *br d*
6	4.06 *dd*	3.68	4.05 *dd*	3.69	4.05 *dd*	3.62	4.07 *dd*
7	3.14 *br t*	2.63	3.11 *br t*	2.67	3.07 *br t*	2.42	3.18 *br t*
8	5.43 *dd*	5.50	4.32 *br t**	4.44	5.20 *dd*	5.20	5.42 *dd*
9	5.02 *br d*	5.02	4.71 *br d**	4.90	4.08 *br d*	3.60	4.98 *br d*
13a	5.64 *d*	5.09	5.75 *d*	5.39	5.61 *d*	5.02	5.71 *br s*
13b	6.31 *d*	6.19	6.39 *d*	6.33	6.29 *br s*	6.16	6.39 *br s*
14	2.00 *br s*	1.58	2.01 *br s*	1.68	1.95 *br s*	1.77	2.04 *br s*
15	1.31 *s*	0.77	1.30 *s*	0.80	1.31 *s*	0.74	1.32 *s*
3′	6.10 *qq*	5.71	6.11 *qq*	5.70	6.13 *qq*	5.71	6.11 *br q*
4′	1.93 *dq*	1.96	1.99 *dq*	2.02	1.97 *dq*	2.00	1.96 *br d*
5′	1.79 *qq*	1.80	1.90 *dq*	1.90	1.86 *qq*	2.00	1.84 *br s*
OAc	2.00 *s*	1.67	—	—	—	—	1.95 *s*

J(Hz): 1,2 *ca* 12.0; 5,6 = 9.6; 6,7 = 5.5; 7,8 = 7.0; 7,13a = 7,13b = 1.1; 8,9 = 10.0; 3′,4′ = 7.0; 3′,5′ = 4′,5′ = 1.5.

*Broadening owing to presence of conformational equilibria.

$[M - 60]^+$, 304 $[M - 100]^+$ and 244 $[M - 160]^+$ corresponded to the loss of the side-chain acids. The ^{1}H NMR spectrum of **1** (C_6D_6, Table 1) displayed the typical signals owing to the exomethylene protons conjugated with the γ-lactone as a pair of downfield finely split doublets at δ5.09 (H-13a) and 6.19 (H-13b) and an upfield broadened doublet of doublets (apparent broad triplet) at δ2.63 (*J* = 7.0, 5.5 Hz) owing to H-7. 2D COSY experiments indicated that the last signal was coupled with the exomethylene signals, as well as to a doublet of doublets at δ3.68 (*J* = 9.6, 5.5 Hz) and a downfield doublet of doublets at δ5.50 (*J* = 10.0, 7.0 Hz) assigning these signals to H-6 and H-8, respectively. The signal at δ3.68 (H-6) was in turn coupled with a broadened doublet at δ2.96 (*J* = 9.6 Hz), and the signal at δ5.50 with a broad doublet at δ5.02 (*J* = 10.0 Hz). Therefore, the signals at δ2.96 and 5.02 must be assigned to H-5 and H-9, respectively. H-1 was located as a broadened doublet at δ5.21 (*J* = *ca* 12.0 Hz) coupled with a broad singlet at δ1.58 (H-14). The sharp singlet at δ0.77 must be from the methyl group at C-4 (H-15) bearing a 4,5-epoxy group. The small $J_{7,13}$ (1.1 Hz, $CDCl_3$) and the large $J_{5,6}$ (9.6 Hz) and $J_{6,7}$ (5.5 Hz) values are typical of 6,12β-germacrolides [2]. Furthermore, the large coupling $J_{7,8}$ (7.0 Hz) and $J_{8,9}$ (10.0 Hz) suggested a *trans-trans* relationship of H-7, H-8 and H-9. The ^{13}C NMR (Table 2) spectrum of karwinsinolide A (**1**) clearly showed 22 carbon resonances. Multipulse APT experiments indicated the presence of five methyl groups, three methylenes, seven CH groups and seven non-protonated carbons. The relative position of the esters was established by NMR correlation with the acetate of **3** (see below).

Table 2. ^{13}C NMR spectral data for **1–4** (50 MHz, $CDCl_3$, chemical shifts referred to $CDCl_3$)

C	1	2	3	4	Multiplicity*
1	132.0	130.4	131.1	131.6	CH
2	24.7	24.6	24.7	24.7	CH_2
3	37.1	37.1	37.1	37.0	CH_2
4	60.3	60.5	60.3	60.3	C
5	61.3	61.5	61.4	61.3	CH
6	68.8	67.7	72.4	68.7	CH
7	44.1	46.3	44.2	44.0	CH
8	78.5	80.8	78.5	78.6	CH
9	77.2	80.1		77.2	CH
10	135.1	134.8	135.4	135.2	C
11	130.6	131.8	132.0	130.3	C
12	169.9	169.6		169.6	C
13	126.1	126.0	125.4	126.0	CH_2
14	19.8	19.9	20.2	19.8	CH_3
15	16.8	16.8	16.8	16.8	CH_3
1′	166.6	167.3		166.8	C
2′	126.7	127.3	126.5	127.1	C
3′	140.0	139.0	140.9	139.1	CH
4′	15.6	15.9	15.8	15.8	CH_3
5′	20.1	20.6	20.2	20.5	CH_3
1″	168.3			166.8	C
2″	20.9			20.7	CH_3

*The number of attached protons were determined from APT and/or DEPT experiments.

The second more polar crystalline lactone was karwinsinolide B (**2**), $C_{20}H_{26}O_6$, $[M]^+$ 362, mp 108–110°. The IR spectrum indicated in addition to the unsaturated γ-lactone and the ester carbonyl, the presence of a hydroxyl group (absorption at 3506 cm^{-1}). The ^{1}H NMR spectrum of **2** (Table 1) showed that an angelate was again present. As the H-8 signal (δ4.32) in the spectrum of **2** was shifted upfield the hydroxyl group can be placed at C-8.

Table 3. ^{1}H NMR spectral data for **6**–**8** (200 MHz) and **9** (500 MHz) ($CDCl_3$, TMS as int. standard)

H	6	7	8	9 ($CDCl_3$)	9 (C_6D_6)
1	1.88 *m*	1.87 *m*	1.88 *m*	1.87 *dt*	1.82 *dt*
2	1.39 *m*	1.40 *m*	1.40 *m*	1.63 *dt*	1.56 *m*
3	1.39 *m*	1.40 *m*	1.40 *m*	2.34 *br t*	1.95
4	3.75 *br sex*	3.75 *br sex*	4.85 *br sex*		
6	2.49 *br t**	2.46 *m**	2.50 *m**	2.45 *br t**	2.30 *m**
7	2.30 *br t**	2.28 *br t**	2.30 *br t**	2.28 *br t**	2.30 *m**
9	2.38 *br q*	2.37	2.36	2.39	2.24
10	1.80 *dd*	1.79 *dd*	1.79 *dd*	1.80 *dd*	1.66 *dd*
10′	1.46 *dd*	1.45 *dd*	1.45 *dd*	1.44 *dd*	1.38 *dd*
12	1.04 *s*	1.05 *s*	1.03 *s*	1.04 *s*	0.94 *s*
13	1.05 *s*	1.05 *s*	1.05 *s*	1.05 *s*	0.89 *s*
14	4.78 *br s*	4.76 *br s*	4.78	4.76	4.81
14′	4.71 *br s*	4.68 *br s*	4.71	4.69	4.71
15	1.18 *d*	1.17 *d*	1.19 *d*	2.11 *s*	1.66 *s*
OAc	—	—	2.03 *s*	—	—
COOMe	—	3.67 *s*	—	3.67 *s*	3.34 *s*

J (Hz): 1,9 = 9,10′ = 10,10′ = 10.0; 9,10 = 8.5; 1,2 = 2,3 = 6,7 = 7.0; 4,5 = 6.2.
*Not first-order pattern, with tendency to an A_2B_2 system.

The third crystalline lactone, karwinsinolide C (**3**), $C_{20}C_{26}O_6$ (CIMS $[M + 1]^+$, 363) mp 210–213°, also contained an angelate ester and a hydroxyl group (IR and ^{1}H NMR spectra). The ^{1}H NMR spectrum indicated that **3** had a 9β-hydroxy group at C-9, as followed from the upfield shift of the H-9 doublet (δ4.08) in the spectrum of **3** compared with those of **1** and **2**.

Acetylation of **2** furnished a monoacetate **4** whose ^{1}H NMR was very similar to, though not identical with, the NMR spectrum of **1**. However, the monoacetate obtained from **3** was identical to **1**, indicating that the acetate ester in karwinsinolide A (**1**) must be at C-9.

The results of a single crystal X-ray analysis (to be published elsewhere) confirmed the relative position of the ester groups, the *E*-configuration of the 1(10) double bond and the synclinal relationship of methyl groups C-4 and C-10 typical of *trans, trans*-germacrolides *cis*-lactonized to C-6.

The seco-caryophyllene-derivative **6** was isolated as a gummy material from the more polar chromatography fractions. The ^{1}H NMR spectrum of **6** (Table 3) clearly indicated the presence of two tertiary methyl singlets at δ1.04 and 1.05 and a secondary methyl doublet at δ1.18 (J = 6.2 Hz). Two one-proton broad singlets at 4.71 and 4.78 suggested the presence of an exomethylene group. A very flat signal at δ4.3-5.1 in addition to IR absorptions at 2500–3500 (broad) and 1711 cm^{-1} indicated the presence of a carboxylic acid which was confirmed by esterification of **6** with diazomethane, giving the methyl ester **7**. A multiplet at δ3.75 (pseudo-sextuplet) was assigned to a proton on a carbon bearing a hydroxyl group. Acetylation of **6** confirmed the above assumption since this signal moved downfield to δ4.85 in the ^{1}H NMR spectrum of **8** (Table 3).

Table 4. ^{13}C NMR spectral data for **6**–**9** (50 MHz, $CDCl_3$, chemical shifts referred to $CDCl_3$)

C	6	7	8	9
1	48.9	48.8	48.6	47.8
2	27.0	27.0	26.5	24.6
3	37.7	37.7	34.2	42.0
4	68.6	68.4	71.2	208.8
5	178.3	173.8	178.9	173.7
6	32.5	32.6	32.4	23.6
7	29.2	29.4	29.1	29.4
8	150.8	151.1	150.7	151.0
9	41.8	41.7	41.6	41.6
10	39.6	39.6	39.6	39.8
11	33.7	33.7	33.7	33.6
12	22.3	22.3	22.2	22.4
13	31.2	31.2	31.2	31.0
14	107.4	107.1	107.3	107.2
15	23.3	23.3	19.8	29.9
OAc	—	—	170.8	—
			21.4	
CO_2Me	—	51.5	—	51.6

2D COSY studies of **6** and derivatives **7** and **8** indicated that the signal at δ3.75 in **6** was coupled with the methyl doublet. Therefore, the hydroxyl group must by placed α to the secondary methyl.

The ^{1}H and ^{13}C NMR (Table 4) spectral data of **6** suggested a sesquiterpenoid with a basic skeleton containing four methyl groups (one of them as an exomethylene) and a carboxylic acid. All these NMR spectral

features resembled those of a 4,5-seco-caryophyllene derivative, similar to compounds **9** and **10** isolated from *Helichrysum diosmitolium* (Inuleae) [3] and *Monactis macbridei* (Heliantheae) [4].

Pyridinium–dichromate oxidation of **7** produced the methyl-ketone **9** confirming the relative position of the secondary methyl group and the hydroxy group. Comparison of the ^{1}H NMR spectral data with values reported for compound **9** [3] revealed their structural identity. ^{1}H and ^{13}C NMR (Table 4) assignments were confirmed by 2D COSY, 2D ^{1}H–^{13}C correlation, inverse long-range ^{1}H–^{13}C correlation and APT NMR methods.

EXPERIMENTAL

Montanoa karwinskii DC. was collected on 29 November 1990 on the Cuernavaca–Tepoztlán road, 14 km E of Cuernavaca in the state of Morelos, México. Voucher specimen No. 550 412 is deposited at the Herbarium of the Instituto de Biologia, UNAM (MEXU) Air-dried leaves (285 g) were extracted at room temp. first, with petrol and then with CH_2Cl_2. Separation of the petrol extract residue (10 g) by CC on silica gel (200 g) using petrol and petrol–EtOAc mixtures of increasing polarity provided 136 frs of *ca* 200 ml each. Known compounds were identified by comparison of spectral data with those of authentic material and/or those reported in the literature. The less polar frs (8–20) gave β-carotene, and mixtures of triterpene esters containing lupeyl, tarasteryl and β-amirin fatty esters (palmitates mainly) and acetates. Frs 2–28 eluted with petrol–EtOAc (19:1) afforded caryophyllene oxide, *ent*-kaurenic acid, β-amirin, sitosterol and stigmasterol. Frs 37–40 eluted with petrol–EtOAc (9:1) contained a mixt. of angeloyl and senecioyl grandifloric acids. Frs 81–85 eluted with petrol–EtOAc (4:1) after prep. TLC (CH_2Cl_2–Me_2CO, 19:1) gave 25 mg of karwinsinolide A (**1**). Successive TLC purifications (CH_2Cl_2–Me_2CO, 19:1, 4×), (petrol–Me_2CO, 7:3, 8×) of frs 96–100 eluted from the CC with petrol–EtOAc (7:3), gave 32 mg karwinsinolide B (**2**) and 12 mg of **5**. Frs 104–110 eluted with petrol–EtOAc (3:2), gave after successive TLC purifications (petrol–EtOAc, 3:2, 5× and CH_2Cl_2–Me_2CO, 19:1, 4×), 15 mg of **2** and 19 mg of karwinsinolide C (**3**) as gummy materials.

The CH_2Cl_2 extract residue (8.3 g) was sepd by CC over silica gel (80 g) using mixts of petrol–EtOAc of increasing polarity, 93 fr. of *ca* 200 ml being collected. Upon further prep. TLC of the various combined frs, the lactones **1–3** were obtained as crystalline compounds. Prep. TLC (CH_2Cl_2–Me_2CO, 19:1) of frs 34–37 gave karwinsinolide A (**1**) (35 mg), mp 204–206° (CH_2Cl_2–Et_2O). Frs 57–60 provided 26 mg of karwinsinolide B (**2**), mp 108–110°. Frs 61–63 gave 38 mg of karwinsinolide C (**3**), mp 210–213°. Frs 64–87 (1.2 g) eluted with petrol–EtOAc (3:2 and 2:3) from the CC were combined and rechromatographed on silica gel providing 136 mg of the seco-caryophyllene derivative **6**. The same sesquiterpene **6** (25 mg) was obtained from the more polar frs of the petrol extract.

Karwinsinolide A (**1**). $C_{22}H_{28}O_7$, crystals, mp 204–206°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1777, 1737, 1720, 1646, 1601. EIMS (probe) 70 eV *m/z* (rel. int.): 404 $[M]^+$ (not observed), 344 $[M - HOAc]^+$ (1), 304 $[M - C_5H_8O_2]^+$ (1), 244 $[M - HOAc - C_5H_8O_2]^+$ (1), 83 $[C_5H_7O]^+$ (100), 55 $[C_4H_7]^+$ (88), 43 $[C_2H_3O]^+$ (75). CIMS (*i*-Bu) *m/z* (rel. int.); 405 $[M + 1]^+$ (6), 345 $[M + 1 - HOAc]^+$ (24), 305 $[M + 1 - C_5H_8O_2]^+$ (7), 245 $[M + 1 - HOAc - C_5H_8O_2]^+$ (39), 227 $[M + 1 - HOAc - C_5H_8O_2 - H_2O)^+$ (17), 83 (100).

Karwinsinolide B (**2**). $C_{20}H_{26}O_6$, crystals, mp 108–110°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3506, 1773, 1713, 1646. EIMS (probe) 70 eV *m/z* (rel. int.): 362 $[M]^+$ (2), 279 $[M - C_5H_7O]^+$ (6), 262 $[M - C_5H_8O_2]^+$ (7), 245 $[M - C_5H_7O_2 - H_2O]^+$ (6), 244 $[M - C_5H_8O_2 - H_2O]^+$ (6), 228 $[M - C_5H_8O_2 - H_2O - O]^+$ (4), 226 $[M - C_5H_8O_2 - 2H_2O]^+$ (3), 217 $[M - C_5H_7O_2 - H_2O - CO]^+$ (5), 83 $[C_5H_7O]^+$ (100), 55 $[C_5H_7]^+$ (26).

Karwinsinolide C (**3**). $C_{20}H_{26}O_6$, crystals, mp 210–213°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3540, 1775, 1715, 1640. EIMS (probe) 70 eV *m/z* (rel. int.): 362 $[M]^+$ (not observed), 262 $[M - C_5H_8O_2]^+$ (0.2), 83 $[C_5H_7O]^+$ (59), 55 $[C_5H_7]^+$ (100). CIMS (*i*-Bu) *m/z* (rel. int.): 363 $[M + 1]^+$ (9), 345 $[M + 1 - H_2O]^+$ (5), 263 $[M + 1 - C_5H_8O_2]^+$ (12), 245 $[M + 1 - H_2O - C_5H_8O_2]^+$ (37), 217 $[M + 1 - H_2O - C_5H_8O_2 - CO]^+$ (14), 101 (23), 83 (100).

Karwinsinolide B acetate (**4**). Sample of **2** (18 mg) was acetylated with Ac_2O–pyridine as usual. TLC (petrol–EtOAc, 7:3, 4×) afforded 12 mg **4**, as oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1776, 1743, 1713, 1646. EIMS (probe) 70 eV *m/z* (rel. int.): 404 $[M]^+$ (not observed), 344 $[M - HOAc]^+$ (0.6), 244 $[M - HOAc - C_5H_8O_2]^+$ (0.4), 83 $[C_5H_7O]^+$ (100), 55 $[C_5H_7]^+$ (42), 43 $[C_2H_3O]^+$ (46). ^{1}H NMR see Table 1.

4-Hydroxy-4,5-seco-caryophyllen-5-oic acid (**6**). Gum. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3165 (broad), 1711, 1642. EIMS (probe) 70 eV *m/z* (rel. int.): 254 $[M]^+$ (not observed), 239 $[M - Me]^+$ (0.3), 236 $[M - H_2O]^+$ (0.3), 221 $[M - Me - H_2O]^+$ (3), 209 $[M - CO_2H]^+$ (0.3), 194 $[M - CO_2H - H_2O - Me]^+$ (3), 191 $[M - CO_2H - H_2O]^+$ (0.3), 176 $[M - CO_2H - H_2O - Me]^+$ (3), 110 (39), 95 (100), 81 (30), 55 (31).

Methyl-4-hydroxy-4,5-seco-caryophyllen-5-oate (**7**). Methylation of **6** (55 mg) with excess of CH_2N_2 in Et_2O provided 48 mg of the ester **7**, after TLC (CH_2Cl_2–Me_2CO, 19:1, 3×) purification, as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1740, 1640. EIMS (probe) 70 eV *m/z* (rel. int.): 288 $[M]^+$ (not observed), 253 $[M - Me]^+$ (0.1), 250 $[M - H_2O]^+$ (0.1), 235 $[M - Me - H_2O]^+$ (1), 126 (29), 110 (49), 95 (100), 79 (46), 55 (39), 45 (82), 41 (90).

4-Acetoxy-4,5-seco-caryophyllen-5-oic acid (**8**). Acetylation of 45 mg of **6** with Ac_2O–pyridine gave after TLC (petrol–EtOAc, 7:3, 3×) purification 40 mg of the acetate **8** as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2500–3500 (br), 1715, 1642. EIMS (probe) 70 eV *m/z* (rel. int.): 269 $[M]^+$ (not observed), 236 $[M - HOAc]^{+\cdot}$ (2), 221 $[M - HOAc - Me]^+$ (2), 110 (28), 95 (39), 55 (26), 43 (100).

Methyl-4-oxo-4,5-seco-caryophyllen-5-oate (**9**). Oxidation of **7** (22 mg) with pyridinium dichromate in CH_2Cl_2 afforded the methyl-ketone **9** as an oil. IR $\nu_{max}^{CHCl_3}$ cm^{-1}:

1731, 1716, 1642. EIMS (probe) 70 eV *m/z* (rel. int.): 266 $[M]^+$ (0.3), 251 $[M - Me]^+$ (3), 223 $[M - MeCO]^+$ (3), 208 $[M - MeCO - Me]^+$ (20), 135 (28), 108 (56), 93 (55), 79 (30), 43 (100).

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