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GUAIANOLIDE-TYPE SESQUITERPENE LACTONES OF *MONTANOA TOMENTOSA* SUBSP. *XANTHIIFOLIA* AND *M. TOMENTOSA* SUBSP. *ROSEI* AND THE MOLECULAR STRUCTURES OF TWO PUMILIN ANALOGS*

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Key Word Index—*Montanoa tomentosa* subsp. *xanthiifolia*; *M. tomentosa* subsp. *rosei*; Asteraceae; Heliantheae; sesquiterpene lactones; guaianolides; X-ray crystal structures.

Abstract—*Montanoa tomentosa* subsp. *xanthiifolia* and *M. tomentosa* subsp. *rosei* produce guaianolides which are very similar to those previously reported from *Berlandiera pumila*, *B. texana* and *B. lyatra*. The molecular structures of 3α-epoxypumilin and 8-acetyl-9-desacylpumilin-9-methacrylate were determined by single crystal X-ray diffraction.

INTRODUCTION

In continuation of our biochemical systematic study of *Montanoa* species, we investigated the sesquiterpene lactones of five collections of *Montanoa tomentosa* Cerv. subsp. *xanthiifolia* (Schultz Bip. in C. Koch) V. A. Funk and one collection of subsp. *rosei* (Rose ex Robins. & Greenm.) V. A. Funk. The major sesquiterpene lactone constituents only differed from pumilin (**1**) and 3α-epoxypumilin (**4**), previously reported from *Berlandiera pumila* and *B. texana* [1], in the ester functions at C-8 and C-9. A heliangolide previously described from *M. tomentosa* subsp. *tomentosa* [2] and other C-5 hydroxylated guaianolides were also present.

In our previous paper [1], the configurations of the epoxide function and the C-5 hydroxyl group of 3-epoxypumilin were not assigned. Therefore, when more material of this compound became available from *Berlandiera lyatra*, single crystal X-ray diffraction studies were performed on this epoxide. In *B. lyatra*, 3α-epoxypumilin (**4**) is the major constituent in addition to pumilin (**1**) [Lee, I. Y. and Fischer, N. H., unpublished observations]. The molecular structure data of 3α-epoxypumilin are included in this paper.

RESULTS AND DISCUSSIONS

8-Acetylpumilin (**2**), $C_{22}H_{24}O_8$, was not immediately comparable with the acetylation product of pumilin (**1**) because of the reported inability to acetylate pumilin using standard procedures [1]. Nevertheless, the ^{1}H NMR spectrum of **2** (Table 1) displayed the signals expected of the acetylation product of pumilin. The upfield shift of H-13a from δ 6.22 (**1**) to 5.50 (**2**) and the loss of geminal coupling between H-13a and H-13b result from the esterification of the α-oriented hydroxyl group at C-8 in **1** [3]. The downfield shift of H-8 from δ 3.93 (**1**) to 5.32 (**2**) and the appearance of an acetate methyl signal at 2.11 are also consistent with the introduction of an acetate at C-8 in **1**.

8-Acetyl-9-desacylpumilin-9-methacrylate (**3**), $C_{21}H_{22}O_8$, mp 222.5–223.5°, produced a ^{1}H NMR spectrum in $CDCl_3$ (Table 1) that differed from the spectrum ($CDCl_3$) of **2** in the substitution of the signals characteristic of a methacrylate moiety for those of an angelate. The ^{1}H NMR spectrum displayed two doublets (J = 3.0 Hz) at δ 5.49 (H-13a) and 6.19 (H-13b) and a doublet of a doublet of a triplet (J = 10, 10, 3 Hz) at 4.09 (H-7) typical of α,β-unsaturated γ-lactones. Irradiation at 4.09 sharpened the two downfield doublets at 5.49 and 6.19 to singlets, simplified a doublet of a doublet (J = 10, 10 Hz) at 5.32 (H-8) to a doublet and collapsed a doublet (J = 10 Hz) at 3.97 (H-6) to a singlet. Irradiation at 5.32 collapsed the signal at 4.09 to a doublet of a triplet (J = 10, 3 Hz) and collapsed the broad doublet (J = 10 Hz) at 6.22 (H-9) to a broad singlet.

The molecular structure of **3** was determined by single crystal X-ray diffraction. These data will be discussed together with the structural data of 3α-epoxypumilin.

8-Acetyl-3α-epoxypumilin (**5**), $C_{22}H_{24}O_9$, exhibits a ^{1}H NMR spectrum ($CDCl_3$, Table 1) which differs from that of **2** in several respects. The H-3 signal has shifted from δ 6.23, a position typical of a hydrogen on an α-carbon of an α,β-unsaturated carbonyl system, to 3.58 which is typical of a hydrogen on a secondary carbon with an oxygen function and the C-14 methyl signal has shifted from 2.27 to 1.80. The latter shift results from the disruption of the cyclopentenone conjugated system caused by the introduction of the 3,4-epoxide. The ^{1}H NMR spectral data of **5** agree with the spectrum expected from the product of the acetylation of 3α-epoxypumilin. The H-13a signal shifts upfield and the geminal coupling between H-13a and H-13b disappears while the H-8 signal shifts downfield from 3.78 (**4**) to 5.26 (**5**) and an acetate methyl signal appears at 2.09 in the spectrum of **5**.

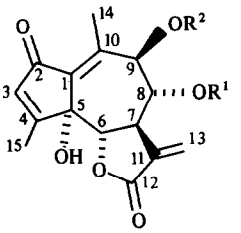
A heliangolide (**8**) isolated from *M. tomentosa* subsp.

*Part 4 in the series "*Montanoa* Terpenes". For part 3 see Seaman, F. C., Malcolm, A. J. and Fischer, N. H., *Phytochemistry*, (in press).

Table 1. ^{1}H NMR data for compounds **2**, **3**, **5**, **6**, **7** and **8** (200 MHz, TMS as internal standard)

	2 ($CDCl_3$)	**2** (Me_2CO-d_6)	**3** ($CDCl_3$)	**3** (Me_2CO-d_6)	**3** (C_6D_6)	**5** ($CDCl_3$)	**6** ($CDCl_3$)	**7** ($CDCl_3$)	**8** (C_6D_6)
H-2	—	—	—	—	—	—	5.64 *m*	5.65 *m*	5.49 *m*
H-3	6.23	6.25	6.19†	6.16	5.95 *br s*	3.58	3.77 *d* (2.0)	—	3.48 *d* (2.0)
H-6	3.96 *d* (11.0)*	4.33 *d* (11.0)	3.97 *d* (10.7)	4.27 *d* (10.5)	4.28 *d* (10.0)	3.98 *d* (10.0)	~ 3.90†	3.90† (10.0)	2.91 *d* (10.0)
H-7	4.12 *ddt* (10.0; 11.0; 3.0)	4.09 *ddt* (10.0; 11.0; 3.0)	4.09 *ddt* (10.7; 10.0; 3.0)	4.08 *ddt* (10.5; 10.0; 3.0)	4.08 *ddt* (10.0; 3.0)	4.15 *ddt* (10.0; 3.0)	~ 3.90†	4.15 *ddt*† (10.0; 10.0; 3.0)	3.97 *ddt* (10.0; 10.0; 3.0)
H-8	5.32 *dd* (10.0)	5.39 *dd* (10)	5.32 *dd* (10.0)	5.4 *dd* (10.0)	5.07 *dd* (10.0)	5.26 *dd* (10.0)	~ 3.90†	5.21 *dd* (10.0; 10.0)	5.10 *dd* (10.0; 10.0)
H-9	6.27 *d* (10.0; 1.5)	6.40 *d* (10.0; 1.5)	6.22 *d* (10.0; 1.0)	6.33 *dd* (10.0; 1.0)	6.20 *brd* (10.0)	6.39 *d* (10.0)	~ 6.20†	6.35 *brd* (10.0)	6.45 *brd* (10.0)
H-13a	6.21 *d* (3.0)	6.08 *d* (3.0)	6.19†	6.09 *d* (3.0)	6.05 *d* (3.0)	6.20 *d* (3.0)	~ 6.20†	5.46 *d* (3.0)	5.25 *d* (3.0)
H-13b	5.50 *d* (3.0)	5.56 *d* (3.0)	5.49 *d* (3.0)	5.55 *d* (3.0)	5.17 *d* (3.0)	5.47 *d* (3.0)	6.20†	6.17 *d* (3.0)	6.13 *d* (3.0)
C-4-Me	2.29 *br s*	2.27 *br s*	2.32 *d* (1.5)	2.3 *d* (1.5)	2.38 *br s*	1.80	1.72	1.63	1.49
C-10-Me	2.33 *br s*	2.40 *br s*	2.23 *d* (1.0)	2.24 *d* (1.0)	1.97 *br s*	2.23 *br s*	1.65 *br s*	1.60 *br s*	1.55 *br s*
OAc	2.11	—†	2.09	2.09	1.62	2.09	2.17	2.05 2.10	1.64 1.68
C-2′-Me	1.92 *br s*	—†	1.95 *br s*	1.96 *dd* (2.0; 1.5)	1.80 *br s*	1.90	2.02 *br s*	1.80–2.0†	1.80–2.0†
C-3′-H_a	6.20†	6.27†	6.19†	6.22 *q* (1.5)	6.16 *br s*	6.25 *br s*	~ 6.20†	5.81 *qq* (7.0; 1.5)	6.20†
C-3′-H_b	—	—	5.72 *dd* (1.5; 1.8)	5.76	5.27 *br s*	2.03 *brs*		1.80–2.0†	1.80–2.0†
C-3′-Me	2.03 *dq* (7.5; 1)	—†	—	—	—	—	2.08 *dq* (7.5; 1.0)	—	—

*Figures in parentheses are coupling constants or line separations in Hz.
†Obscured by other signals.



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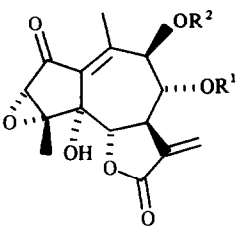
2 $R^1 = Ac$, $R^2 = Ang$

3 $R^1 = Ac$, $R^2 = Mac$



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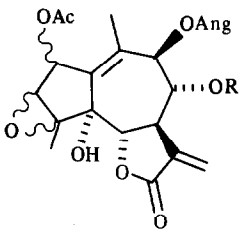
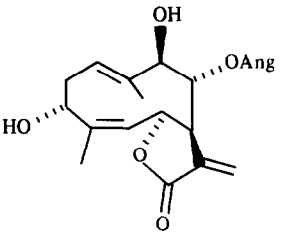
5 $R^1 = Ac$, $R^2 = Ang$



R

6 H

7 Ac



8

xanthiifolia produced spectral data identical to those reported for zoapatanolide A (9β-hydroxy-3-epinobilin) from *M. tomentosa* subsp. *tomentosa* [2].

Montanoa tomentosa subsp. *rosei* produced as a major sesquiterpene lactone constituent **7**, the ^{1}H NMR spectrum (Table 1) of which is identical to the C-8 acetylation product of zoapatanolide C (**6**) which was recently reported from *M. tomentosa* subsp. *tomentosa* [4].* Based on ^{1}H NMR (Table 1) and mass spectral experimental data, **7** is also present in *M. tomentosa* subsp. *xanthiifolia*.

Single crystal X-ray diffraction data

3α-Epoxypumilin (**4**). The structure of 3α-epoxypumilin (Fig. 1) closely resembles that of pumilin, with which it is isomorphous. The present study confirms the basic skeleton, and establishes both the 3,4-epoxy function and the hydroxyl group at C-5 to be α-oriented. Although the precision of the present determination is slightly higher, details of the structure of the pumilin skeleton have been described fully, and only differences between pumilin and 3α-epoxypumilin will be discussed here. The three atoms of the epoxy group form a perfect equilateral triangle within experimental error, having side 1.452(3) Å. The plane of this triangle forms an angle of 95.3° with the best plane of the cyclopentanone ring. Individual bond distances and angles agree generally well with those of pumilin except for expected differences associated with epoxidation, and in the region of the angelate substituent.

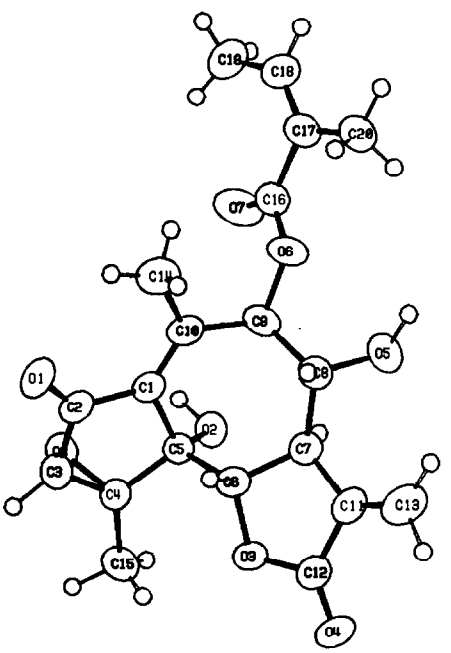


Fig. 1. Molecular structure of 3α-epoxypumilin.

Pumilin exhibits some unusual features in the angelate group; particularly the C-17 to C-18 bond is shortened to 1.206(9) Å, attributed to high thermal motion. Thermal motion in 3α-epoxypumilin is substantially lower, and the

*We thank Dr. Leovigildo Quijano for making available spectral data prior to publication [4].

C-17 to C-18 distance, 1.312(5) Å, is normal for a double bond.

In pumilin, the only intermolecular contact described as a hydrogen bond was O2-H ... O1, having an O ... O separation of 2.78 Å, and an angle about H of 160°. That hydrogen bond is also present in 3α-epoxypumilin, but is longer [O ... O 2.869(3) Å, O–H ... O 165°], due to the presence of the epoxide function, which makes a close contact [O1 ... O8 2.895(3) Å] not present in pumilin. In addition, 3α-epoxypumilin exhibits a strong hydrogen bond involving the hydroxyl group O5 and lactone carbonyl O4 of a neighboring molecule, with O ... O 2.792(3) Å and O–H ... O angle 164°. In pumilin, the O4 ... O5 contact is even shorter, 2.72 Å, but the position located for the hydroxyl H atom is not indicative of a hydrogen bond. Due to the facts that this hydrogen atom was successfully refined in the present structure, and that its refined position is quite plausible in terms of hydrogen bonding, we feel that its location is probably more reliable for *both* structures than that determined in the pumilin crystal structure.

8-*Acetyl-9-desacylpumilin-9-methacrylate* (**3**). The skeletal structure of **3** (Fig. 2) agrees well with those of pumilin and 3α-epoxypumilin, as seen by the torsion angles in Tables 3 and 5. The largest difference in an analogous torsion angle between the two structures reported here is only 10.5°, C4-C5-C1-C2. The methacrylate substituent is ordered in the *s-trans* conformation with a slight twist about its central bond (O7-C18-C19-C20 torsion angle 9.4°). The most notable intermolecular contact is a hydrogen bond involving hydroxyl group O3 as donor and carbonyl oxygen atom O4 as acceptor, analogous to the similar interaction in 3α-epoxypumilin. The O ... O distance here is 2.749(4) Å, and the O–H ... O angle is 138°.

EXPERIMENTAL

Chemical data. For general procedures see ref. [5]. NMR spectra were recorded on a Hitachi–Perkin Elmer R600A 60 MHz and a Brucker 200 MHz FT spectrometer. X-Ray data were obtained from an Enraf–Nonius CAD-4 automatic diffractometer.

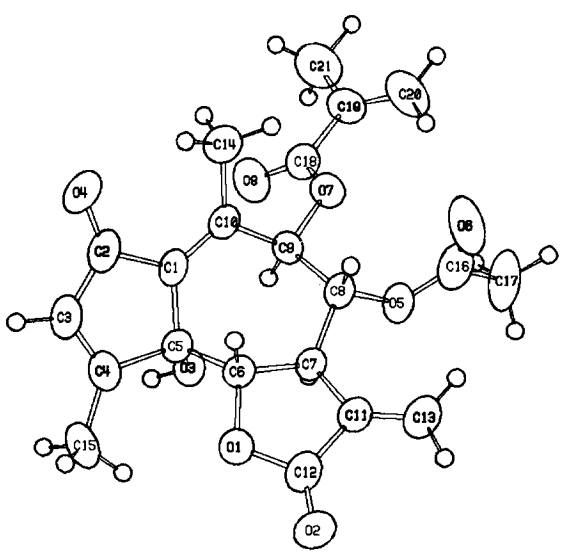


Fig. 2. Molecular structure of 8-acetyl-9-desacylpumilin-9-methacrylate.

Montanoa tomentosa subsp. *xanthiifolia* (F2802, 33 g) was collected 60 miles west of Ciudad Valles on a highway 70 side road to Cardenas (San Luis Potosi, Mexico) on 11 November 1978. The voucher has been deposited at the Ohio State University Herbarium (OS). The whole dried leaf, stem and head material were extracted twice in CH_2Cl_2 for 2 min and worked up in the usual fashion [5] to yield 0.64 g syrup. The syrup was chromatographed by preparative TLC (silica gel G, 0.5 mm × 20 × 20 cm; $CHCl_3$–Me_2CO, 9 : 1) to yield 8 bands. Band 4, when rechromatographed using the same conditions, produced 2 bands, the second of which contained **5**. Further preparative TLC of band 6 yielded pure **2**, and band 7 contained **6**. Compounds **2** (8 mg) and **8** (10 mg) were also isolated by preparative TLC from a CH_2Cl_2 extract of another *M. tomentosa* subsp. *xanthiifolia* collection, F2872 (31.5 g) collected 10.9 miles south-east of Izucar de Matamoros (Puebla, Mexico) on 22 November 1978 (0.70 g crude syrup). F2872 has also been deposited at OS.

Collection Fri2846 (OS) from 3.5 miles north of Zumpango del Rio (Guerrero, Mexico; 16 November 1978) consisted of 45.5 g of whole dried leaf, stem and head material which when extracted by the above procedure yielded 1.34 g of crude syrup. Preparative TLC of this syrup using the above procedure yielded 5 bands. Band 3 contained 13 mg **3**. Compound **3** was also isolated from FT 2813 (OS, 36.5 g) collected near Jacala, Hidalgo, Mexico on 12 November 1978.

Montanoa tomentosa subsp. *rosei* collection FCa3005 (OS) was collected east of Los Lomas off the highway to Alamos on 21 December 1978 in Sinaloa, Mexico. Dried leaf material (36.5 g) was extracted (CH_2Cl_2) and chromatographed over silica gel in $CDCl_3$ and Me_2CO with increasing proportions of Me_2CO. Fractions 9–12 yielded a compound which upon further preparative TLC was identified as **7** (7 mg).

8-*Acetylpumilin* (**2**). $C_{22}H_{24}O_8$, gum, UV λ_{max}^{MeOH} nm(ε): 203 (2.23 × 10^4); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3500 (hydroxyl), 1770 (γ-lactone), 1750, 1720 (esters), 1690 (α,β-unsaturated ketone), 1640, 1620 (double bonds); EIMS (probe) 70 eV *m/z* (rel. int.): 416 $[M]^+$ (0.4), 398 $[M-H_2O]^+$ (1.9), 356 $[M-C_2H_4O_2]^+$ (0.2), 338 $[M-H_2O-C_2H_4O_2]^+$ (3.0), 316 $[M-C_5H_8O_2]^+$ (1.3), 298 $[M-H_2O-C_5H_8O_2]^+$ (0.4), 274 $[M-C_5H_8O_2-CH_2CO]^+$ (2.7), 257 $[M-C_2H_4O_2-C_5H_7O_2]^+$ (13.1), 256 $[M-C_2H_4O_2-C_5H_8O_2]^+$ (5.2), 238 $[M-H_2O-C_2H_4O_2-C_5H_8O_2]^+$ (8.3), 83 $[C_5H_7O]^+$ (100), 55 $[C_4H_7]^+$ and 43 $[MeCO]^+$ (15.0). [Calc. for $C_{22}H_{22}O_7$ $(M-H_2O)$: 398.1366. Found: (MS) 398.1360.]

8-*Acetyl-9-desacylpumilin-9-methacrylate* (**3**). $C_{21}H_{22}O_8$, mp 222.5–223.5°, UV λ_{max}^{MeOH} nm(ε): 203 (1.8 × 10^4); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3490 (hydroxyl), 1758 (γ-lactone), 1718, 1710 (esters), 1675 (α,β-unsaturated ketone), 1625, 1605 (double bonds; EIMS (probe) 70 eV *m/z* (rel. int.): 402 $[M]^+$ (0.8), 384 $[M-H_2O]^+$ (4.6), 360 $[M-C_2H_2O]^+$ (2.2), 342 $[M-C_2H_4O_2]^+$ (0.9), 324 $[M-C_2H_4O_2-H_2O]^+$ (5.9), 316 $[M-C_4H_6O_2]^+$ (1.4), 298 $[M-H_2O-C_4H_6O_2]^+$ (0.5), 292 (4.2), 291 $[M-C_2H_2O-C_4H_5O]^+$ (10.1), 274 $[M-C_2H_2O-C_4H_6O_2]^+$ (3.4), 273 $[M-C_2H_2O-H_2O-C_4H_5O]^+$ (5.7), 257 $[M-C_2H_4O_2-C_4H_5O_2]^+$ (22.4), 256 $[M-C_4H_6O_2-C_2H_4O_2]^+$ (16.9), 238 $[M-C_4H_6O_2-C_2H_4O_2-H_2O]^+$ (13.3), 69 $[C_4H_5O]^+$ (100), 43 $[MeCO]^+$ (15.7) and 41 $[C_3H_5]^+$ (14.2). [Calc. for $C_{21}H_{22}O_8$: 402.1315. Found: (MS) 402.1324. Calc. for $C_{21}H_{20}O_7$ $(M-H_2O)$: 384.1208. Found: (MS) 384.1223. Calc. for $C_{19}H_{20}O_7$ $(M-C_2H_2O)$: 360.1208. Found: (MS) 360.1249. Calc. for $C_{19}H_{18}O_6$ $(M-C_2H_4O_2)$: 342.1102. Found: (MS) 342.1092. Calc. for $C_{19}H_{16}O_5$ $(M-C_2H_4O_2-H_2O)$: 324.0997. Found: (MS) 324.0956. Calc. for $C_{15}H_{16}O_6$ $(M-CH_2CO$

$-C_4H_4O$): 292.0945. Found: (MS) 292.0936. Calc. for $C_{15}H_{15}O_6$ ($M-CH_2CO-C_4H_5O$): 291.0867. Found: (MS) 291.0866. Calc. for $C_{15}H_{14}O_5$ ($M-C_2H_2O-C_4H_6O_2$): 247.0840. Found: (MS) 274.0851. Calc. for $C_{15}H_{13}O_4$ ($M-C_2H_4O_2-C_4H_5O_2$): 257.0813. Found: (MS) 257.0811. Calc. for $C_{15}H_{10}O_3$ ($M-C_4H_6O_2-C_2H_4O_2-H_2O$): 238.0629; Found: (MS) 238.0612.]

8-*Acetyl-3α-epoxypumilin* (**5**). $C_{22}H_{24}O_9$, gum, UV λ_{max}^{MeOH} nm (ε): 203 (1.7×10^4); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3555 (hydroxyl), 1770 (γ-lactone), 1715 (esters), 1625 (double bonds); EIMS (probe) 70 eV *m/z* (rel. int.): 432 $[M]^+$ (0.3), 390 $[M-C_2H_2O]^+$ (0.3), 372 $[M-C_2H_4O_2]^+$ (0.3), 354 $[M-C_2H_4O_2-H_2O]^+$ (0.1), 332 $[M-C_5H_8O_2]^+$ (0.5), 314 $[M-C_5H_8O_2-H_2O]^+$ (0.1), 272 $[M-C_5H_8O_2-C_2H_4O_2]^+$ (1.4), 254 $[M-C_5H_8O_2-C_2H_4O_2-H_2O]^+$ (0.5), 244 $[M-C_5H_8O_2-C_2H_4O_2-CO]^+$ (1.2), 229 $[M-C_5H_8O_2-C_2H_4O_2-CO-Me]^+$ (1.0), 83 $[C_5H_7O]^+$ (100), 55 $[C_4H_7]^+$ (25.8) and 43 $[MeCO]^+$ (16.6). CIMS (*i*-butane) *m/z* 433 $[M+1]^+$.

Zoapatanolide C (**6**) [4]. EIMS (probe) 70 eV *m/z* (rel. int.): 434 $[M]^+$ (not observed), 334 $[M-C_5H_8O_2]^+$ (0.3), 292 $[M-C_5H_8O_2-C_2H_2O]^+$ (0.5), 274 $[M-C_5H_8O_2-C_2H_4O_2]^+$ (1.3), 256 $[M-C_5H_8O_2-C_2H_4O_2-H_2O]^+$ (1.0).

9β-Hydroxy-3-epinobilin (**8**). $C_{20}H_{26}O_6$, gum, UV λ_{max}^{MeOH} nm (ε): 201 (1.5×10^4); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3410 (OH), 1745 (γ-lactone), 1700 (ester); EIMS (probe) 70 eV *m/z* (rel. int.): 362 $[M]^+$ (not observed), 344 $[M-H_2O]^+$ (0.7), 262 $[M-C_5H_8O_2]^+$ (1.8), 244 $[M-C_5H_8O_2-H_2O]^+$ (3.1), 216 $[M-C_5H_8O_2-H_2O-CO]^+$ (1.8), 207 (3.9), 189 (3.3), 179 (5.3), 165 (5.0), 149 (5.9), 121 (3.7), 83 (100), 55 (14.9); ^1H NMR (200 MHz, $CDCl_3$, TMS): δ 5.32 (*t*, $J_{1,2}$ = 7.5 Hz, H-1), 2.17 (*ddd*, $J_{2a,2b}$ = 13.0 Hz, $J_{2a,3}$ = 12.0 Hz, $J_{2a,1}$ = 7.5 Hz, H-2a), 2.66 (*ddd*, $J_{2b,2a}$ = 13.0 Hz, $J_{2b,3}$ = 5.0 Hz, $J_{2b,1}$ = 7.5 Hz, H-2b), 4.73 (*dd*, $J_{3,2a}$ = 12.0 Hz, $J_{3,2b}$ = 5.0 Hz, H-3), 5.11 (*br d*, $J_{5,6}$ = 10.0 Hz, H-5), 4.75 (*br d*, $J_{6,5}$ = 10.0 Hz, $J_{6,7}$ = 1.0 Hz, H-6), 2.77 (*br d*, $J_{7,8}$ = 9.5 Hz, H-7), 4.99 (*dd*, $J_{7,8}$ = 9.5 Hz, $J_{8,9}$ = 9.5 Hz, H-8), 4.12 (*d*, $J_{8,9}$ = 9.5 Hz, H-9), 5.59 (*br s*, H-13a), 6.28 (*br s*, H-13b), 1.88 (*br s*, H-14), 1.78 (*br s*, H-15), 6.12 (*qq*, $J_{3',4'}$ = 7.0 Hz. $J_{3',2'\text{-Me}}$ = 1.0 Hz, H-3'), 1.90 (*q*, $J_{2'\text{-Me},3'}$ = 1.0 Hz, C-2'-Me) and 1.95 (*qd*, $J_{4',3}$ = 7.0 Hz, $J_{4',2'\text{-Me}}$ = 1.0 Hz, H-4'). [Calc. for $C_{20}H_{24}O_5$ ($C_{20}H_{26}O_6-H_2O$): 344.1624. Found: (MS) 344.1643. Calc. for $C_{15}H_{18}O_4$ ($M-C_5H_8O_2$): 262.1204. Found (MS) 262.1203. Calc. for $C_{15}H_{16}O_3$ ($M-C_5H_8O_2$): 244.1099. Found: (MS) 244.1080. Calc. for $C_{15}H_{14}O_2$ ($M-C_5H_8O_2-2H_2O$): 226.0993. Found: (MS) 226.0954.]

X-Ray data. Intensity data for both compounds were collected on an Enraf–Nonius CAD4 diffractometer equipped with MoKα radiation (λ = 0.71073 Å) and a graphite monochromator. The $\omega-2\theta$ scans were made at variable rate, designed to yield $I \simeq 50\sigma(I)$ for all significant reflections. For each compound, one octant of data having angular limits listed below was measured. Crystal data for 3α-epoxypumilin (**4**) are: $C_{20}H_{22}O_8$, MW = 390.4, orthorhombic space group $P2_12_12_1$, a = 7.999(2), b = 13.421(2), c = 18.013(2) Å, Z = 4, d_c = 1.341 g/cm^3, μ(MoKα) = 0.97 cm^{-1}, angular limits $1° \leqslant \theta \leqslant 25°$. Crystal data for 8-acetyl-9-desacylpumilin-9-methacrylate (**3**) are: $C_{21}H_{22}O_8$, MW = 402.4, orthorhombic space group $P2_12_12_1$, a = 6.713(2), b = 10.924(2), c = 28.511(4) Å, Z = 4, d_c = 1.278 g/cm^3, μ(MoKα) = 0.92 cm^{-1}, angular limits $1° \leqslant \theta \leqslant 27°$. For compound **3**, 1461 of the 1964 unique data had $I > 3\sigma(I)$ and were used in the refinement. For compound **4**, 1385 of the 2199 unique data were used.

Due to the similarity in the cell dimensions of compound **4** with those of pumilin, it was assumed that the epoxide function does not alter the packing mode, and the basic skeleton of

Table 2. Coordinates for 3α-epoxypumilin

Atom	*x*	*y*	*z*	*B* or B_{eq}	Atom	*x*	*y*	*z*	*B* or B_{eq}
O1	0.3008 (3)	0.6850 (2)	0.5879 (1)	5.00 (5)	C18	0.7626 (5)	0.2568 (3)	0.4049 (2)	5.89 (9)
O2	0.4917 (3)	0.7598 (2)	0.3426 (1)	3.87 (4)	C19	0.9166 (6)	0.3039 (4)	0.4357 (2)	7.9 (1)
O3	0.1221 (3)	0.8155 (2)	0.3142 (1)	4.20 (5)	C20	0.4779 (6)	0.2379 (3)	0.3521 (2)	5.32 (8)
O4	−0.0848 (3)	0.8275 (2)	0.2314 (1)	6.07 (6)	H20	0.594 (5)	0.788 (4)	0.360 (3)	9.9 (13)
O5	0.2837 (4)	0.4964 (2)	0.2488 (1)	5.85 (6)	H50	0.236 (5)	0.438 (3)	0.250 (3)	10.2 (14)
O6	0.4509 (3)	0.4346 (2)	0.3672 (1)	4.84 (5)	H3	0.280 (4)	0.885 (2)	0.553 (2)	4.2 (7)
O7	0.7190 (3)	0.4700 (2)	0.3855 (2)	7.33 (8)	H6	0.109 (4)	0.712 (3)	0.391 (2)	6.5 (9)
O8	0.4927 (3)	0.8594 (2)	0.4899 (1)	4.65 (5)	H7	0.315 (3)	0.677 (2)	0.263 (1)	2.3 (5)
C1	0.3719 (4)	0.6773 (2)	0.4562 (2)	3.57 (6)	H8	0.176 (3)	0.514 (2)	0.343 (2)	4.2 (7)
C2	0.3296 (4)	0.7241 (3)	0.5287 (2)	3.98 (7)	H9	0.499 (4)	0.575 (2)	0.343 (2)	3.4 (6)
C3	0.3276 (4)	0.8344 (3)	0.5174 (2)	4.38 (7)	H131	−0.055 (4)	0.547 (3)	0.231 (2)	6.8 (10)
C4	0.3524 (4)	0.8565 (2)	0.4389 (2)	3.99 (7)	H132	−0.154 (4)	0.639 (3)	0.211 (2)	6.8 (9)
C5	0.3597 (4)	0.7578 (2)	0.3953 (2)	3.49 (6)	H141	0.375	0.521	0.551	5.0
C6	0.1988 (4)	0.7324 (2)	0.3551 (2)	3.73 (6)	H142	0.447	0.451	0.498	5.0
C7	0.2112 (4)	0.6526 (2)	0.2955 (2)	3.76 (6)	H143	0.257	0.474	0.501	5.0
C8	0.2534 (4)	0.5460 (2)	0.3171 (2)	4.14 (7)	H151	0.332	1.020	0.439	5.0
C9	0.4112 (4)	0.5394 (2)	0.3657 (2)	4.13 (7)	H152	0.204	0.957	0.386	5.0
C10	0.3867 (4)	0.5788 (2)	0.4440 (2)	3.92 (7)	H153	0.390	0.965	0.363	5.0
C11	0.0501 (4)	0.6695 (3)	0.2560 (2)	4.61 (7)	H18	0.773	0.186	0.404	5.0
C12	0.0158 (5)	0.7773 (3)	0.2635 (2)	4.51 (7)	H191	0.957	0.270	0.473	5.0
C13	−0.0586 (5)	0.6084 (3)	0.2257 (3)	7.9 (1)	H192	0.899	0.370	0.453	5.0
C14	0.3675 (5)	0.5024 (3)	0.5035 (2)	5.78 (9)	H193	1.008	0.307	0.399	5.0
C15	0.3140 (6)	0.9544 (3)	0.4042 (2)	5.73 (9)	H201	0.500	0.166	0.348	5.0
C16	0.6087 (5)	0.4092 (3)	0.3778 (2)	4.66 (8)	H202	0.441	0.261	0.305	5.0
C17	0.6263 (5)	0.2982 (3)	0.3787 (2)	4.97 (8)	H203	0.385	0.245	0.386	5.0

Estimated standard deviations in the least significant digits are shown in parentheses.

pumilin was used as a beginning model. The epoxy oxygen atom and angelate side chain were located by Fourier techniques. Hydrogen atoms were located in difference maps, and those of the hydroxyl groups and on carbon atoms through C-13 were refined isotropically; other hydrogen atoms were included as fixed contributions with $B = 5.0$ Å^2. Refinement was carried out by full matrix least squares, treating non-hydrogen atoms anisotropically, and convergence was achieved with $R = 0.037$ and $Rw = 0.055$ for observed data. Refined coordinates are given in Table 2, and selected torsion angles are listed in Table 3. Uncertainties in distances are 0.003–0.006 Å, those in angles are 0.2–0.4°, and those for torsion angles are 0.4–0.7°.

The structure of **3** was solved by direct methods (MULTAN) and refined in a fashion similar to that employed for compound **4**. All hydrogen atoms were located by difference maps, and included as fixed contributions with $B = 5.0$ Å^2. Convergence was achieved with $R = 0.056$ and $Rw = 0.068$ for observed data. Refined coordinates are given in Table 4, and selected torsion angles are listed in Table 5. Uncertainties are 0.005–0.008 Å for distances, 0.3–0.7° for angles, and 0.5–1.0° for torsion angles. A final difference map exhibits evidence of some rotational disorder of both skeletal methyl groups.

Table 3. Selected torsion angles for 3α-epoxypumilin

Atoms	Angle (°)	Atoms	Angle (°)
C5-C1-C2-C3	−12.0	C8-C9-C10-C1	−72.4
C1-C2-C3-C4	5.1	C9-C10-C1-C5	6.5
C2-C3-C4-C5	3.8	O3-C6-C7-C11	−38.8
C3-C4-C5-C1	−10.7	C6-C7-C11-C12	31.2
C4-C5-C1-C2	13.8	C7-C11-C12-O3	−11.8
C10-C1-C5-C6	63.0	C11-C12-O3-C6	−14.3
C1-C5-C6-C7	−83.5	C12-O3-C6-C7	34.1
C5-C6-C7-C8	66.0	C8-C9-O6-C16	153.2
C6-C7-C8-C9	−51.7	O6-C16-C17-C18	−164.4
C7-C8-C9-C10	71.2	C16-C17-C18-C19	−0.8

Table 4. Coordinates for non-hydrogen atoms of 8-acetyl-9-desacylpumilin-9-methacrylate

Atom	x	y	z	Atom	x	y	z
O1	0.1847 (6)	0.1116 (3)	0.6290 (1)	C8	0.3403 (8)	0.4379 (5)	0.6498 (2)
O2	−0.0015 (7)	0.0536 (4)	0.6899 (2)	C9	0.5124 (8)	0.4628 (4)	0.6161 (2)
O3	0.6060 (6)	0.1914 (3)	0.6041 (1)	C10	0.4602 (8)	0.4446 (5)	0.5648 (2)
O4	0.3795 (6)	0.3642 (4)	0.4644 (1)	C11	0.1354 (9)	0.2603 (5)	0.6858 (2)
O5	0.4094 (7)	0.4728 (3)	0.6960 (1)	C12	0.0902 (10)	0.1307 (5)	0.6707 (2)
O6	0.2261 (9)	0.6436 (4)	0.6961 (2)	C13	0.0374 (12)	0.3128 (6)	0.7193 (2)
O7	0.5731 (6)	0.5868 (3)	0.6251 (1)	C14	0.4308 (10)	0.5587 (5)	0.5355 (2)
O8	0.8735 (7)	0.5443 (4)	0.5954 (1)	C15	0.4129 (13)	−0.0185 (5)	0.5526 (2)
C1	0.4352 (8)	0.3313 (5)	0.5479 (2)	C16	0.3499 (11)	0.5775 (6)	0.7137 (2)
C2	0.3973 (8)	0.2961 (5)	0.4982 (2)	C17	0.4603 (13)	0.6034 (7)	0.7587 (2)
C3	0.3871 (9)	0.1635 (5)	0.4974 (2)	C18	0.7622 (10)	0.6160 (5)	0.6133 (2)
C4	0.4063 (9)	0.1140 (5)	0.5399 (2)	C19	0.8113 (10)	0.7445 (5)	0.6248 (2)
C5	0.4341 (9)	0.2140 (4)	0.5770 (2)	C20	0.6888 (13)	0.8128 (6)	0.6501 (3)
C6	0.2550 (8)	0.2278 (5)	0.6103 (2)	C21	1.0033 (14)	0.7915 (7)	0.6062 (3)
C7	0.3013 (8)	0.3005 (5)	0.6549 (2)				

Estimated standard deviations in the least significant digits are shown in parentheses.

Table 5. Selected torsion angles for 8-acetyl-9-desacylpumilin-9-methacrylate

Atoms	Angle (°)	Atoms	Angle (°)
C5-C1-C2-C3	−3.4	C8-C9-C10-C1	−72.7
C1-C2-C3-C4	2.3	C9-C10-C1-C5	6.5
C2-C3-C4-C5	−0.1	O1-C6-C7-C11	−37.9
C3-C4-C5-C1	−2.0	C6-C7-C11-C12	31.2
C4-C5-C1-C2	3.3	C7-C11-C12-O1	−13.3
C10-C1-C5-C6	62.5	C11-C12-O1-C6	−12.1
C1-C5-C6-C7	−84.2	C12-O1-C6-C7	31.9
C5-C6-C7-C8	69.4	C8-C9-O7-C18	156.2
C6-C7-C8-C9	−57.3	C9-C8-O5-C16	102.4
C7-C8-C9-C10	74.6	O7-C18-C19-C20	9.4

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