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The isolation and structure determination of two new guaianolides, pumilin and its 2,3-epoxide, from *Berlandiera pumila* and *B. texana* are reported. The structure of pumilin was determined from nmr and mass spectral data, and from an X-ray single crystal study; the structure of the epoxide was found by comparison of nmr spectra. Pumilin is shown to be a  $\Delta^{1(10)}$ -cis-guaianolide with a cyclopentenone ring attached to C1 and C5, and an  $\alpha$ -methylene- $\gamma$ -lactone ring *trans*-fused to C6 and C7. The absolute configuration was inferred from spectral considerations and knowledge of previous structural determinations. The cd spectrum of pumilin exhibits a negative Cotton effect, and the lactone chromophore has left-handed chirality. The cycloheptene ring is in the chair configuration, with the lactone a half-chair and the cyclopentenone essentially planar. Crystals are orthorhombic,  $a = 7.065$ ,  $b = 13.652$ ,  $c = 19.586$  Å, space group  $P2_12_12_1$ ,  $Z = 4$ , and the final R value is 3.9%. The crystal structure is strengthened by an O...O hydrogen bond linking the molecules into infinite chains.

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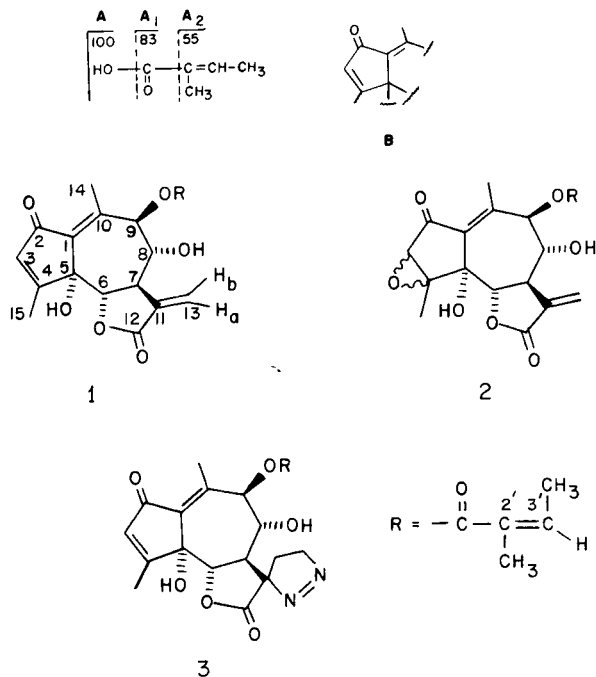
## Introduction.

In our biochemical systematic study of the subtribe Melampodiinae, tribe Heliantheae (Compositae) (1,2) we were interested to learn more about the chemical constituents of the genus *Berlandiera* since this taxon had recently been removed from the subtribe Melampodiinae and placed into the newly established subtribe Engelmanniinae Stuessy (3). Previously, two guaianolides had been isolated from *B. subacaulis* (Nutt.) Nutt. Which resembled constituents found in *Artemisia* and related genera (4). We now wish to report the results of our chemical investigation of *Berlandiera pumila* and *B. texana* which resulted in two new guaianolides. The new compounds were characterized by chemical and spectral methods and the molecular structure of pumilin was determined by single crystal x-ray diffraction.

## Results and Discussion.

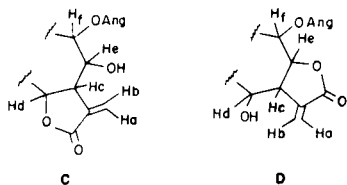
### A. Chemical and Spectroscopic Characterizations.

Standard column chromatography procedures applied to extracts of dried aerial parts of *B. pumila* provided a colorless, crystalline compound which we named pumilin (**1**),  $C_{20}H_{22}O_7$ , mp 244-245° dec. The uv ( $\lambda$  max 257 nm) and ir (1680, 1640 and 1620  $cm^{-1}$ ) absorptions were characteristic of the dienone chromophore (**B**) present in a number of guaianolides (5). The nmr signals at 2.42 (C-4-Me), 2.61 (C-10-Me) and 6.33 ppm (H-3) also supported a cyclopentenone (**B**) moiety in pumilin.



The presence of hydroxyl(s) and an  $\alpha$ -methylene- $\gamma$ -lactone moiety was indicated by ir bands at 3460 and 1775  $cm^{-1}$ , respectively. An absorption at 1715  $cm^{-1}$  suggested an additional ester function in the molecule. The nmr spectrum and ms data corroborated the above assignments. A series of diagnostic signals, a one-proton quartet of a quartet at 5.98 ppm (H-3',  $J_{H-3',3'-CH_3} = 7.5$  Hz;  $J_{H-$

${}^3J_{3'}\text{-CH}_3 = 1.5 \text{ Hz}$ ) and two methyl-absorptions, a broadened quartet at 1.97 ppm (C-2'-CH<sub>3</sub>) and a doublet of a quartet at 2.02 ppm (C-3'-CH<sub>3</sub>), suggested the presence of an angelate moiety in **1**. This was supported by a series of strong ms peaks at *m/e* 274 (M-A), 83 (A<sub>1</sub>) and 55 (A<sub>2</sub>). Further assignments of the basic skeleton of pumilin were deduced from extensive double resonance experiments in pyridine-d<sub>5</sub>. Irradiation of the multiplet at 4.51 ppm (H<sub>c</sub>) removed the large couplings of the two allylicly coupled protons at 6.46 and 6.60 ppm (H<sub>a</sub> and H<sub>b</sub>), respectively, collapsed the doublet at 4.13 ppm (H<sub>d</sub>) to a singlet and simplified the broadened doublet of doublets at 4.22 ppm (H<sub>e</sub>) to a doublet. When the signal at 4.22 ppm (H<sub>e</sub>) was irradiated the broadened doublet at 6.98 ppm (H<sub>f</sub>) collapsed to a broadened singlet. On the basis of the above chemical shifts and coupling data the partial structures **C** and **D** can be formulated. It was hoped that upon acetylation of pumilin the hydrogen attached to the carbon carrying the



hydroxyl group would shift downfield, allowing an unambiguous decision between partial formulae **C** and **D**. Attempts to prepare pumilin acetate with acetic anhydride/pyridine resulted in decomposition of the substrate. However, preparation of the pyrazoline derivative (**3**) allowed assignment of H<sub>e</sub> and H<sub>f</sub> in the spectrum indicating that H<sub>e</sub>, a doublet at 4.96 ppm (*J* = 10.5 Hz) was shifted considerably farther downfield than H<sub>f</sub> at 3.78 ppm suggesting that H<sub>e</sub> represent the lactonic proton and H<sub>f</sub>

the one attached to the hydroxyl-containing carbon. This excluded partial structure **D** and by combining fragments **B** and **D** allowed the formulation of a guaianolide skeleton for pumilin. The only position for attachment of the unassigned oxygen in pumilin could be at C-5. This led to formula **1** exclusive of the stereochemistry at C-5 to C-9. Assuming that H-7 be  $\alpha$  as in all sesquiterpene lactones from higher plants (6), the configurations at C-6 to C-9 could be derived from the <sup>1</sup>H nmr couplings which were correlated with the dihedral angles obtained from stereo-model considerations. The large coupling between H-6 and H-7 (*J*<sub>6,7</sub> = 10.5 Hz) suggested an antiperiplanar orientation of the two nuclei, that is, H-6 being  $\beta$  or the presence of a *trans*-6,12-lactone in **1**. A negative band at 268 nm in the cd spectrum of **1** supported this assignment (7) although it is known that this criterion does not hold at all times (8). Further large couplings near 10 Hz between H-7 and H-8 as well as H-8 and H-9 also suggested anti-periplanar hydrogens at these centers from which H-8 $\beta$  and H-9 $\alpha$  configurations were derived. Further evidence for an  $\alpha$ -oriented OH group at C-8 was provided by the geminal coupling between the two C-13 protons together with a paramagnetic shift of H-13 below 6 ppm (9). The configuration of the OH group at C-5 could not be derived from nmr parameters of **1**. Since well-formed single crystals of pumilin could be obtained, final configurational and conformational details were resolved by x-ray studies which will be discussed later.

Extracts of *B. texana* provided upon silica gel chromatography pumilin and a minor constituent which differed from the empirical formula of pumilin by one additional oxygen, C<sub>20</sub>H<sub>22</sub>O<sub>8</sub>, mp 178-183°.

Comparison of the nmr spectrum of the new compound with that of pumilin allowed assignment of its structure.

Table I

<sup>1</sup>H-NMR Parameters (a) of Pumilin (**1**), 3,4-Epoxypumilin (**2**) and the Pyrazoline (**3**)

	<b>1</b>	<b>2</b>	<b>3</b>
H-3	6.33 [6.22] q (1.5)	3.87 [3.78]	6.15 br
H-6	4.13 [3.93] (c) d (10.5)	4.24 [3.93] (c) d (10.5)	4.94 d (10.5)
H-7	4.51 [3.93] (c) dddd (3.0; 3.5; 10; 10.5)	4.61 [3.93] (c) dddd (3.0; 3.5; 10; 10.5)	3.53 dd (10; 10.5)
H-8	4.22 [3.93] brdd (10; 10)	[3.93] (c)	3.78 dd (10; 10.5)
H-9	6.98 [6.1] brd (10)	7.11 [6.25] (c) brd (10)	5.93 brd (10)
H-13a	6.46 [6.22] (c) dd (3.0; 1.5)	6.46 [6.25] (c) dd (3.5; 1.5)	
H-13b	6.60 [6.22] (c) dd (3.0; 1.5)	6.56 [6.25] (c) dd (3.0; 1.5)	2.05 m (b)
C-4-Me	2.42 [2.33] d (1.5)	1.93 [1.8]	2.14 br
C-10-Me	2.61 [2.30] br	2.46 [2.22] br	2.33 br
C-3'-H	5.98 [6.22] (c) qq (7.5; 1.5)	5.95 [6.25] (c) qq (7.2; 1.5)	6.21 qq (7.0; 1.5)
C-2'-Me	1.97 [2.02] brq (1.5)	1.92 [2.05] brq (1.5)	1.90 br
C-3'-Me	2.02 [2.03] dq (7.5; 1.5)	2.03 [2.01] dq (7.2; 1.5)	1.98 br
C-13-CH <sub>2</sub>	--	--	4.74 dd (7.0; 8.0)

(a) The spectrum of **1** and **2** were run at 200 MHz in pyridine-d<sub>5</sub> and deuteriochloroform and **3** at 270 MHz in deuteriochloroform with TMS as internal standard. The data given in brackets for compounds **1** and **2** were obtained in deuteriochloroform. Chemical shifts ( $\delta$ ) are in parts per million; coupling constants or line separations are given in parenthesis; multiplicities are designated as follows: d, doublet; q, quartet; m, multiplet with center given; br, broadened signal. (b) Obscured by other signals. (c) Part of a complex multiplet.

Table 2  
Summary of Data Collection and Processing Parameters

Space Group	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
Cell Constants	a = 7.065(4) Å b = 13.652(4) c = 19.586(5) V = 1889.1 Å <sup>3</sup> Z = 4 molecules/cell
Molecular Weight	MW = 374.39 g·mole <sup>-1</sup>
Density (calc)	ρ = 1.32 g·cm <sup>-3</sup>
Absorption Coefficient	μ = 0.66 cm <sup>-1</sup>
Data Collection Range	4.0° ≤ 2θ ≤ 48.0°
Scan Width	Δθ = 1.00 + 0.35 tanθ°
Maximum Scan Time	300 sec
Scan Speed Range	0.30 to 3.35° min <sup>-1</sup>
Total Data Collected	2473
Data with I > 3σ(I)	1042
Total Variables	308
R = Σ  F <sub>o</sub>  - F <sub>c</sub>   /Σ F <sub>o</sub>	0.039
R <sub>w</sub> = [Σw( F <sub>o</sub> - F <sub>c</sub>  ) <sup>2</sup> /Σw F <sub>o</sub>   <sup>2</sup> ] <sup>1/2</sup>	0.027
Weights	w = σ( F ) <sup>-2</sup>

Major portions of the spectrum were very similar except that the lowfield narrow quartet at 6.33 ppm assigned to H-3 in **1** was replaced by a sharp singlet at 3.87 ppm in the new compound. Furthermore, instead of the C-4-methyl absorption at 2.42 ppm in **1**, compound **2** exhibited a three-proton singlet at 1.93 ppm. This strongly suggested that the new minor constituent represented a 3,4-epoxide derivative of pumilin. The configurations at the centers C-6 to C-9 in **2** were found to be the same as in pumilin (**1**) on the basis of the <sup>1</sup>H nmr couplings of **2** (see Table 1). The configurations at C-2, C-3 and C-5 of **2** remain open.

### B. X-Ray Crystal Structure of Pumilin.

Figure 2 shows the β-face of the skeleton of pumilin, a Δ<sup>1(10)</sup>-cis-guaianolide with an α-methylene-γ-lactone trans-fused at C-6 and C-7. The absolute configuration could not be determined experimentally due to the lack of an anomalous scatterer, and was instead assigned based on the assumption that the C-7 side chain has the customary equatorial β-orientation found in those guaianolides for which the absolute stereochemistry has been established (4). The hydrogen positions, as well as the OH group on C-8, are then seen to be in the same orientations suggested by the nmr interpretation. The cycloheptene ring is in the

chair configuration, as found in similar structures (8,10), and in keeping with the observations of Herz, *et al.*, (4) who noted that all guaianolides of the chair type have H-7 and H-8 *trans*. There is a slight distortion to the chair, as shown by the torsion angles about the C-1, C-10 double bond (see Table 6), however the seven torsion angles of the ring are still in very good agreement with the theoretical values derived for a perfect C<sub>s</sub>-chair (11). The bond distances in the cycloheptene ring are very nearly ideal for C-C single and double bonds, and compare favorably with previous determinations (8,10).

The cyclopentenone ring is essentially flat, the average of the endocyclic torsion angle moduli being only 5°. The bond distances are not remarkable, with perhaps the exception of C-2, C-3 which is slightly shorter than expected for a C(s<sub>p</sub><sup>2</sup>)-C(s<sub>p</sub><sup>2</sup>) bond and O-1, C-2, which is slightly long. This indicates some possible resonance through the C-2, C-3 area, which is as expected. There are examples in other natural products, however, in which this is not the case (12).

The α-methylene-γ-lactone ring is decidedly non-planar, as evidenced by the sum of the five endocyclic torsion angle moduli (138°). Much of this is due to the *trans*-fused orientation; however, other examples have been seen to have sums as low as 73° (13). The sum of the moduli in *cis*-fused lactones is generally much smaller *eg.* 39° in parthemollin (14). As mentioned above, the cd spectrum showed a negative band at 268 nm (see Figure 1), indicative of a negative Cotton effect of the n→π\* transition, and therefore a *trans*-fused lactone at C-6. The presence of a cyclopentenone chromophore frequently interferes with this method (7), however, and so care had to be taken in our interpretation initially. The crystal structure shows the lactone chromophore to have left-handed chirality (negative C:O-C:C torsion angle), and Beecham has suggested that the sign of the Cotton effect is determined by

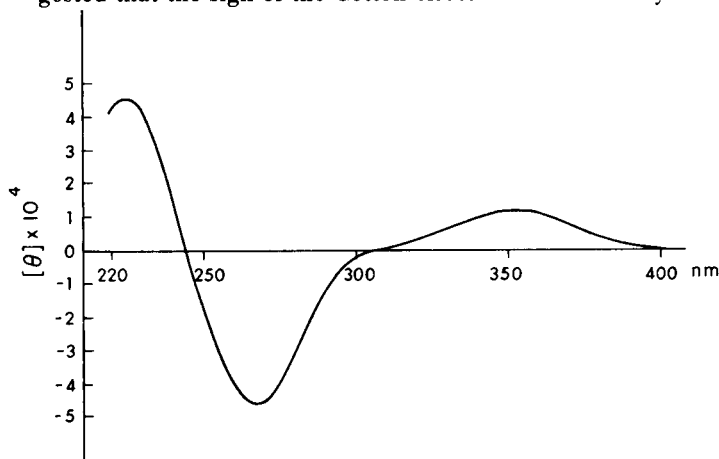


Figure 1. The cd spectrum of Pumilin. The n→π\* transition of the α-methylene-γ-lactone chromophore occurs at 268 nm.

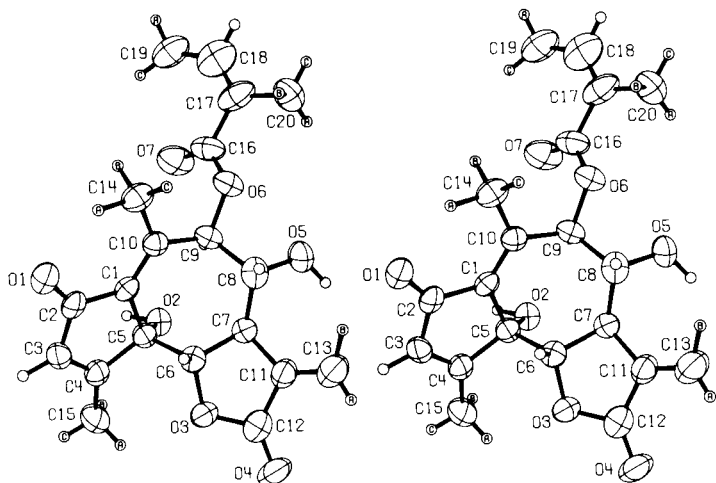


Figure 2. Stereoscopic view of the atom labelling scheme for Pumilin. The thermal ellipsoids are 40% equiprobability envelopes. Hydrogens are shown as spheres of arbitrary diameter, with numbers corresponding to the atoms to which they are attached.

this (15). Cox and Sim further show that the exocyclic C:C-C:O and endocyclic  $C_{\alpha}$ - $C_{\beta}$ - $C_{\gamma}$ -O torsion angles are highly correlated ( $-15^{\circ}$  vs.  $-41^{\circ}$  in the present case), and they suggest that this may be a more sensitive indicator of the sign of the Cotton effect (16). Our data is consistent with each of the above theories, and thus the weight of evidence for our assumption of the absolute configuration shown in Figure 2 is overwhelming. The bond distances and angles in the ring are quite consistent with values found in other sesquiterpenoid lactones (8,10,13,17), as well as with the parameters given for  $\alpha$ -methyltetronic acid (18).

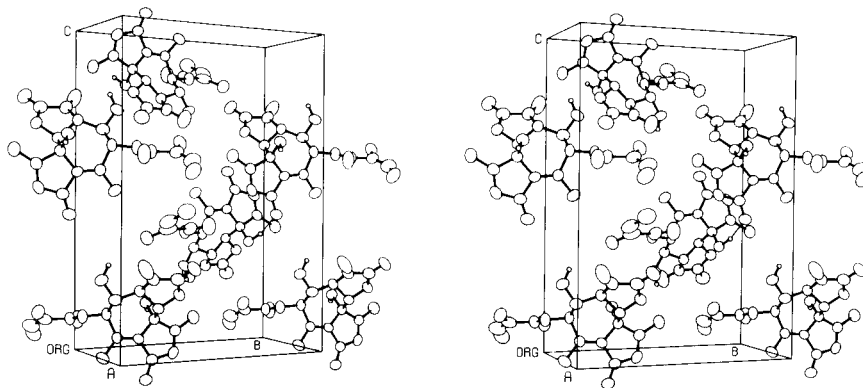


Figure 3. Stereoscopic packing diagram as viewed into the  $a$  axis. Only the alcoholic hydrogens are included. A thin solid line indicates the O1...O2 intermolecular hydrogen bond.

The angelate ( $C_4H_7COO$ ) group attached to the C-9 position shows some unusual features. The short C-16, O-6 bond is probably due to resonance with O-6. The exceptionally short C-17, C-18 double bond is obviously not sensible from any chemical argument, and can only be attributed to the lack of a correction for thermal libration in the atomic positions. The same would hold true for C-8, O-5. Figure 3 shows a view of the molecular packing of pumilin in the unit cell, including the hydrogen bonding between molecules which tends to link them together into chains. The O-2...O-1 hydrogen bond is a strong one, having an O...O separation of 2.78 Å. The angle at H-2 is  $160^{\circ}$ .

## EXPERIMENTAL

### A. Chemical and Spectral Data.

A collection of *Berlandiera pumila* (Michx) Nutt. (F. Seaman and E. Olivier, No. 331) was made on May 2, 1978, 9.9 miles west of San Augustine on State Highway 21, San Augustine County, Texas. Voucher specimens are deposited at the Louisiana State University Herbarium at Baton Rouge, Louisiana. Dried leaves (500 g) were extracted and worked up as previously described (19) providing 6.9 g of crude syrup which was chromatographed over silica gel using mixtures of petroleum ether and ether with increasing amounts of ether. Intermediate fractions provided a crystalline material (150 mg) which after recrystallization from ethyl acetate gave pure pumilin (1),  $C_{20}H_{22}O_7$ , mp 244-245°, dec, (maroon color); uv  $\lambda$  max (methanol) 257 nm ( $\epsilon = 8,400$ ); cd:  $[\theta]_{222} + 4.6 \times 10^4$ ;  $[\theta]_{268} - 4.7 \times 10^4$ ;  $[\theta]_{300} 0$ ;  $[\theta]_{351} + 2 \times 10^4$ ; ir (potassium bromide):  $\nu$  max 3460 (OH), 1775 ( $\gamma$ -lactone), 1715 (ester), 1680 (cyclopentenone), 1640 (double bond), 1620 (cisoid double bond); ms: (intensity, assignments) 374 (1.0, M<sup>+</sup>), 356 (1.8, M-H<sub>2</sub>O), 338 (1.6, M-2H<sub>2</sub>O), 291 (6.1, M-A<sub>1</sub>), 274 (4.6, M-A), 256 (3.6, M-A-H<sub>2</sub>O), 228 (1.8, M-A-H<sub>2</sub>O-CO), 200 (1.1, M-A-H<sub>2</sub>O-2CO), 185 (1.0, M-A-H<sub>2</sub>O-2CO-CH<sub>3</sub>), 178 (2.5), 165 (1.2), 161 (13.2), 150 (3.4), 83 (100 A<sub>1</sub>), 69 (5.5), 55 (15.8, A<sub>2</sub>).

### Pyrazoline (3).

Treatment of pumilin (1) with diazomethane in ether provided compound 3, gum; ms (Cl, NH<sub>3</sub>): 434 (2, M + NH<sub>4</sub><sup>+</sup>), 420 [5, (M + NH<sub>4</sub><sup>+</sup>) - CH<sub>2</sub>], 417 (7, MH<sup>+</sup> - CH<sub>2</sub>), 406 [78, (M - NH<sub>4</sub><sup>+</sup>) - N<sub>2</sub>], 389 (16, MH<sup>+</sup>-CO), 371

Table 3  
Atomic Coordinates and Thermal Parameters (X1000)

Atom	X/A	Y/B	Z/C	U11	U22	U33	U12	U13	U23
O1	.3284(5)	.6949(3)	.5677(2)	50(3)	88(3)	55(2)	4(2)	1(2)	-1(2)
O2	.5435(6)	.7464(3)	.3430(2)	49(3)	66(3)	59(3)	-12(2)	9(2)	-2(2)
O3	.1299(6)	.8027(2)	.3075(2)	58(3)	63(2)	63(2)	3(2)	-9(2)	8(2)
O4	-.0919(7)	.8138(3)	.2253(2)	82(4)	109(4)	86(3)	21(3)	-29(3)	17(3)
O5	.3022(6)	.4798(3)	.2622(2)	114(4)	78(3)	56(2)	9(3)	-9(3)	-17(2)
O6	.4828(7)	.4303(3)	.3740(2)	78(4)	47(3)	90(3)	7(2)	0(3)	1(2)
O7	.7848(6)	.4695(3)	.3956(3)	58(3)	85(4)	157(4)	10(3)	-5(4)	0(3)
C1	.3900(7)	.6738(4)	.4461(2)	37(4)	62(4)	45(3)	0(3)	-4(3)	5(3)
C2	.3507(8)	.7290(4)	.5097(3)	25(3)	77(5)	55(4)	0(3)	-8(3)	-2(4)
C3	.3484(8)	.8322(4)	.4921(3)	43(4)	67(4)	71(4)	13(3)	-8(3)	-19(4)
C4	.3685(8)	.8462(4)	.4257(3)	45(4)	65(4)	60(4)	1(3)	-7(3)	-5(4)
C5	.3840(8)	.7482(4)	.3887(3)	50(4)	55(4)	53(3)	-1(3)	0(4)	-2(3)
C6	.2036(8)	.7225(4)	.3487(3)	55(4)	55(4)	51(4)	-4(3)	2(4)	5(3)
C7	.2308(9)	.6407(4)	.2961(3)	61(4)	55(4)	51(4)	0(4)	-8(4)	3(3)
C8	.2673(11)	.5357(5)	.3209(3)	66(5)	72(5)	60(4)	-16(4)	6(4)	-2(4)
C9	.4393(10)	.5326(4)	.3685(3)	56(4)	40(4)	74(4)	1(3)	4(4)	3(3)
C10	.4079(7)	.5768(4)	.4398(3)	43(4)	53(3)	55(4)	0(3)	-3(3)	2(3)
C11	.0501(10)	.6570(5)	.2558(3)	72(5)	65(4)	70(4)	-6(4)	-18(4)	6(4)
C12	.0134(11)	.7634(5)	.2580(3)	57(5)	89(6)	64(4)	-7(4)	-3(4)	5(4)
C13	-.0644(15)	.5970(6)	.2247(5)	131(8)	83(6)	150(8)	-8(6)	-79(7)	5(6)
C14	.3965(11)	.5069(5)	.4978(3)	72(5)	76(5)	66(4)	-4(4)	-2(4)	18(4)
C15	.3864(14)	.9409(5)	.3875(5)	109(8)	51(4)	98(6)	1(5)	-18(7)	-3(5)
C16	.6641(13)	.4075(5)	.3868(4)	89(7)	62(5)	81(5)	26(5)	20(5)	10(4)
C17	.6808(12)	.2955(6)	.3861(3)	83(6)	132(7)	62(4)	49(6)	14(4)	23(5)
C18	.8216(15)	.2603(6)	.4109(4)	108(8)	135(8)	93(6)	17(7)	29(6)	37(5)
C19	.9936(13)	.3021(8)	.4427(4)	75(6)	133(7)	118(8)	20(6)	-30(5)	26(6)
C20	.5063(12)	.2354(6)	.3566(4)	81(6)	74(5)	100(6)	5(5)	7(5)	-15(5)
H2	.645(10)	.780(4)	.368(3)	120					
H3	.332	.887	.527	45(14)					
H5	.257	.501	.218	120					
H6	.108(7)	.708(3)	.386(2)	58(15)					
H7	.329(8)	.668(4)	.261(3)	98(22)					
H8	.161(7)	.510(3)	.342(2)	50(16)					
H9	.540(6)	.566(3)	.345(2)	32(14)					
H13A	-.170(10)	.626(5)	.201(3)	131(29)					
H13B	-.050(9)	.521(4)	.239(3)	120					
H14A	.345(8)	.545(4)	.544(3)	100					
H14B	.533	.487	.517	100					
H14C	.299(9)	.455(4)	.488(3)	102(25)					
H15A	.299(10)	.952(4)	.352(3)	111(28)					
H15B	.555(12)	.948(5)	.379(4)	201(42)					
H15C	.362(8)	.993(3)	.414(2)	72(20)					
H18	.822	.188	.412	150					
H19A	1.062(10)	.244(4)	.470(3)	150					
H19B	1.080(11)	.316(6)	.413(4)	150					
H19C	.989(12)	.369(5)	.468(3)	150					
H20A	.498(12)	.265(5)	.315(4)	150					
H20B	.406(11)	.235(5)	.392(4)	150					
H20C	.551(11)	.173(5)	.355(4)	150					

(5, MH<sup>+</sup> · CO · H<sub>2</sub>O), 306 (10, 406 · A), 289 (8, 389 · A); 271 (7, 389 · A · H<sub>2</sub>O), 253 (9, 389 · A · 2H<sub>2</sub>O), 227 (9, 271 · CO<sub>2</sub>), 198 (100, 406 · CO · CO<sub>2</sub> · 2H<sub>2</sub>O), 180 (61), 144 (12), 83 (8, A<sub>1</sub>) 55 (74, A<sub>2</sub>).

Dried aerial part (250 g) of *Berlandiera texana* DC. (C. Newsom, collected on July 1, 1979 in Travis County, Texas; voucher is deposited at the Ohio State University Herbarium, Columbus, Ohio) were extracted and worked up as described before (19) giving 3.1 g of crude syrup which upon silica gel chromatography (petroleum ether-ether) provided 200 mg of pumilin (1) and from less polar fractions 14 mg of epoxide (2), C<sub>20</sub>H<sub>22</sub>O<sub>8</sub>, mp 178-183° dec; uv (methanol): λ max 253 nm (ε, 2,400); 203 nm (ε, 7,100); ir: ν max 3440 (OH), 1765 (γ-lactone), 1710 (ester), 1680 sh (cyclopentenone) 1620-1640 broad (double bonds), 1255 (epoxide); ms: (in-

tensity, assignments) 390 (0.2, M<sup>+</sup>), 374 (0.1, M-O), 354 (0.3, M-2H<sub>2</sub>O), 308 (0.7, M-A<sub>1</sub>), 291 (4.4, M-A-H or M-A<sub>1</sub>-O), 277 (1.6), 261 (1.0), 244 (0.7, M-A-H<sub>2</sub>O-CO), 216 (0.6, M-A-H<sub>2</sub>-2CO), 195 (3.3), 177 (2.9), 165 (9.2), 161 (1.2), 149 (2.5), 128 (1.7), 83 (100, A<sub>1</sub>), 69 (8.5), 55 (25.5, A<sub>2</sub>).

Anal. Calcd. for C<sub>15</sub>H<sub>15</sub>O<sub>6</sub> (M-C<sub>5</sub>H<sub>7</sub>O<sub>2</sub>): M<sub>r</sub> = 291.0867. Found: M<sub>r</sub> (ms) = 291.0862.

#### B. X-Ray Data.

A pale yellow, tabular crystal of approximate dimensions 0.4 × 0.5 × 0.9 mm was used for data collection. All measurements were made on an Enraf-Nonius CAD-4 automatic diffractometer using Mo K<sub>α</sub> radiation monochromatized by a dense graphite crystal assumed to be ideally imperfect. Lattice constants and an orientation matrix were obtained from a least squares fit of 25 centered reflections. Final cell constants are given in Table 2, along with other pertinent data. The Laue symmetry was determined to be mmm, and from the systematic absences noted the space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> was indicated.

Intensities were measured using the θ-2θ scan technique, with the scan rate depending directly on the net count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every two hours of exposure time as a check of electronic reliability and crystal stability, and no abnormalities were noted. One eighth of the reciprocal sphere was collected such that each of h, k, and l was non-negative, according to the limits given in Table 2. Lorentz and polarization factors were applied in reducing the intensities to structure factor amplitudes, but no absorption correction was deemed necessary. All data having I > 3σ (I) were used in least squares refinement, with the exception of 40 reflections found to be poorly determined, possibly due to extinction, and which are available from the authors.

Table 4

Bond Lengths (Å)

C1-C2	1.483(7)	C17-C18	1.206(9)
C1-C5	1.516(7)	C17-C20	1.590(11)
C1-C10	1.336(5)	C18-C19	1.480(12)
C2-O1	1.237(6)	O1...H2	1.85
C2-C3	1.450(7)	O2-H2	0.98(7)
C3-C4	1.323(6)	C3-H3	1.02
C4-C5	1.526(7)	O5-H5	0.97
C4-C15	1.500(9)	C6-H6	1.01(5)
C5-O2	1.439(6)	C7-H7	1.04(6)
C5-C6	1.536(7)	C8-H8	0.93(5)
C6-C7	1.532(7)	C9-H9	0.96(4)
C6-O3	1.457(6)	C13-H13A	0.96(6)
C7-C8	1.536(8)	C13-H13B	1.08(5)
C7-C11	1.518(8)	C14-H14A	1.11(5)
C8-C9	1.532(8)	C14-H14B	1.07
C8-O5	1.402(6)	C14-H14C	1.01(6)
C9-C10	1.538(7)	C15-H15A	0.95(6)
C9-O6	1.434(6)	C15-H15B	1.21(8)
C10-C14	1.486(7)	C15-H15C	0.90(4)
C11-C12	1.476(7)	C18-H18	0.98
C11-C13	1.303(9)	C19-H19A	1.08(6)
C12-O3	1.381(7)	C19-H19B	0.87(7)
C12-O4	1.198(7)	C19-H19C	1.04(6)
C16-C17	1.534(9)	C20-H20A	0.92(7)
C16-O6	1.341(8)	C20-H20B	1.00(7)
C16-O7	1.214(8)	C20-H20C	0.91(6)

Table 5

Bond Angles (°) (a)

C2-C1-C5	106.2(5)	C7-C8-O5	106.1(5)
C2-C1-C10	126.8(5)	C9-C8-O5	110.1(6)
C5-C1-C10	126.7(5)	C8-C9-C10	115.2(5)
C1-C2-O1	127.1(5)	C8-C9-O6	104.1(5)
C1-C2-C3	107.2(4)	C10-C9-O6	110.2(5)
O1-C2-C3	125.6(5)	C9-C10-C1	119.2(5)
C2-C3-C4	111.9(5)	C9-C10-C14	116.7(5)
C3-C4-C5	110.4(5)	C14-C10-C1	124.1(5)
C3-C4-C15	128.6(6)	C7-C11-C12	106.1(6)
C5-C4-C15	120.9(5)	C7-C11-C13	132.4(7)
C4-C5-C1	103.6(4)	C12-C11-C13	121.6(7)
C4-C5-C6	112.5(5)	C11-C12-O3	107.4(6)
C4-C5-O2	111.5(5)	C11-C12-O4	131.2(7)
C1-C5-C6	104.4(5)	O3-C12-O4	121.5(6)
C1-C5-O2	115.4(4)	C12-O3-C6	108.1(4)
C6-C5-O2	109.2(4)	C9-O6-C16	116.3(5)
C5-C6-C7	113.9(5)	O6-C16-O7	122.4(6)
C5-C6-O3	114.0(5)	O6-C16-C17	107.6(7)
C7-C6-O3	102.7(4)	O7-C16-C17	130.0(8)
C6-C7-C8	119.3(5)	C16-C17-C18	117.2(10)
C6-C7-C11	97.9(5)	C16-C17-C20	117.3(7)
C8-C7-C11	116.3(5)	C18-C17-C20	125.4(9)
C7-C8-C9	110.6(5)	C17-C18-C19	133.9(10)

(a) The angles involving the hydrogens range from 112° to 127° for sp<sup>2</sup> carbons, and from 97° to 121° for sp<sup>3</sup>-hybridized atoms, with estimated standard deviations of about 5°.

Table 6

Selected Torsion Angles (°)

O2-C5-C1-C2	130.04	C1-C5-C6-C7	-83.99
O2-C5-C1-C10	-56.10	C1-C10-C9-C8	-71.25
O2-C5-C6-O3	-77.50	C2-C1-C5-C6	-110.09
O2-C5-C6-C7	39.94	C2-C1-C10-C9	177.08
O3-C6-C5-C1	158.58	C5-C1-C10-C9	4.46
O3-C6-C5-C4	46.84	C5-C6-O3-C12	159.79
O3-C6-C7-C8	-167.13	C5-C6-C7-C8	69.05
O4-C12-C11-C13	-15.22	C5-C6-C7-C11	-164.81
O5-C8-C7-C11	68.06	C6-C5-C1-C10	63.77
O5-C8-C9-O6	-49.75	C6-C5-C4-C15	-76.60
O5-C8-C9-C10	-170.48	C6-C7-C8-C9	-55.65
O6-C9-C8-C7	-166.69	C7-C8-C9-C10	72.57
O6-C9-C10-C14	-9.47	C8-C9-O6-C16	152.27
O6-C16-C17-C18	-164.31	C8-C9-C10-C14	107.88
O6-C16-C17-C20	12.44	C9-O6-C16-C17	-176.46
O7-C16-O6-C9	2.51	C10-C9-O6-C16	-83.65
O7-C16-C17-C18	16.83	C16-C17-C18-C19	-1.10
O7-C16-C17-C20	-166.42	C19-C18-C17-C20	-177.55
Cyclopentenone Ring:		Lactone Ring:	
C1-C2-C3-C4	4.16	C6-C7-C11-C12	33.14
C2-C3-C4-C5	1.12	C7-C11-C12-O3	-13.29
C3-C4-C5-C1	-5.73	C11-C12-O3-C6	-14.40
C4-C5-C1-C2	7.88	C12-O3-C6-C7	36.09
C5-C1-C2-C3	-7.55	O3-C6-C7-C11	-40.99

The structure was solved using MULTAN (20), which revealed all but one of the non-hydrogen atoms in the best E-map. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were located in difference density maps. Some of the thermal parameters of hydrogens were unreasonably large and had to be fixed. The positions of H-3, H-14B, and H-18 refined poorly and were thus held constant at ideally calculated values. H-5 tended to refine to an unusually short distance from O-5, and was fixed at a position further out along the O-5 to H-5 vector, a position which made chemical sense sterically. Those parameters which were held constant have no esd in Table 3. After all shift/esd ratios were less than 0.1, the refinements converged to the agreement factors listed in Table 2. The atomic scattering factors for the non-hydrogen atoms were computed from numerical Hartree-Fock wave functions (21); for hydrogen those of Stewart, Davidson, and Simpson (22) were used. All calculations were done using the SHELX-76 series of programs of G. M. Sheldrick (23). No unusually high correlations were noted between any of the independent variables. Final positional and thermal parameters are listed in Table 3, with bond lengths and angles given in Tables 4 and 5 based on these positions. Table 6 contains selected torsion angles. The numbering scheme is shown in stereo in figure 2, with unlabelled hydrogens having numbers corresponding to the atoms to which they are bonded.

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