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SESQUITERPENE LACTONES FROM *PARTHENIUM TOMENTOSUM**

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Key Word Index—*Parthenium tomentosum*; Heliantheae; Compositae; sesquiterpene lactones; pseudoguaianolides; xanthanolides.

Abstract—Four populations of *Parthenium tomentosum* var. *tomentosum* were examinated. In addition to the known lactones, ivalbatine, acetyl ivalbatine, parthomentine, incanine and ligulatine C, three new pseudoguaianolides: 4-*O*-desacetyl ligulatine C; 1-dehydroperuvinine and parthoximentine were also isolated. Chemical and spectroscopic methods were used for their structural determination.

INTRODUCTION

The chemical investigations of the perennial species *Parthenium tomentosum* var. *tomentosum* have resulted in the isolation of several sesquiterpene lactones with pseudoguaiane and xanthane skeletons [1–5]. We report here the chemical composition of four populations of this species which afforded eight lactones. Three of them are new natural products.

RESULTS AND DISCUSSION

From aerial parts of *P. tomentosum* collected near Teotitlán del Camino, Oaxaca, three sesquiterpene lactones were isolated. The less polar one was identified by comparison with the reported physical constants, as the xanthanolide acetyl ivalbatine (**1**) previously described as a component of *P. fruticosum* var. *trilobatum* [3]. The second compound was an oil with spectroscopic features identical to those for ivalbatine (**2**) obtained from *Iva dealbata* [6]. Xanthanolides **1** and **2** were correlated by acetylation.

The third and more polar component isolated from this collection was formulated as $C_{15}H_{18}O_4$ (**3**). This compound exhibited IR absorptions at 3530 cm^{-1} (hydroxyl) 1760, 1655 cm^{-1} (α,β-unsaturated-γ-lactone) and 1710 cm^{-1} (cyclopentenone). The presence of the last group was confirmed by the UV absorption at 224 nm (ε = 7866). The ^1H NMR spectrum (Table 1) showed at high field a singlet (δ1.26, 3H) and a doublet (δ1.36, J = 7 Hz, 3H), due to tertiary and secondary methyl groups, respectively. The co-occurrence of these groups along with the cyclopentenone allowed us to propose a pseudoguaiane skeleton for **3**. The ^1H NMR spectrum also exhibited two doublets at δ6.29 ($J_{7,13}$ = 2.5 Hz) and 5.63 ($J_{7,13'}$ = 2 Hz) for the vinylic protons conjugated with the γ-lactone. The proton on the lactone closure appeared as a *ddd* signal (δ4.55, J = 11, 7.5 and 4 Hz). Therefore the lactone must be closed to C-8 with a β-orientation. The double bond conjugated with the ketone was located at C-1, since the ^1H NMR spectrum showed a signal at δ6.02 for the vinylic proton at C-2. The presence of a broad singlet at δ4.08, which sharpened upon D_2O addition and shifted downfield to δ5.39 in the acetyl derivative **4** suggested the presence of a secondary hydroxyl group at C-4. The chemical shift of the methyl group at C-5 in **3** suggests a *cis*-relationship with the C-4 hydroxyl, which was confirmed by the magnitude of the induced shift of the C-5 methyl group when the spectra of **3** were determined using $CDCl_3$–TMS solution containing $Eu(fod)_3$ (Table 1). Taking into account the β-orientation of the C-5 and C-10 methyl groups in all the parthenolides, the C-4 hydroxyl must be β-oriented as is depicted in **3**.

From a second plant collection made in Mitla, Oaxaca, four sesquiterpene lactones were isolated. The most abundant one was identified as incanine, a pseudoguaianolide which was formulated as **5**. The proposed position of the carbonyl group at C-4 in this compound was based on biogenetic grounds only [7]. In order to have a chemical proof for this formulation, incanine was oxidized under Baeyer–Villiger conditions yielding the dilactone **6** whose IR spectrum showed a band at 1710 cm^{-1} due to the δ-lactone and in its ^1H NMR spectrum (Table 2) the signals for the C-15 protons appeared at lower field than those of incanine. The production of **6** corroborated the structure **5** for incanine.

The second lactone isolated from this population was identified as ligulatine C (**7**) by comparison of their spectroscopic data [8], but the secondary acetoxy group was located tentatively at C-4 with no definitive stereochemistry.

In order to clarify these points, ligulatine C was correlated with incanine as follows. Incanine (**5**) was reduced with sodium borohydride affording two products **8** and **10**. The major one was the dihydroderivative **8**, which exhibited a hydroxyl absorption at 3570 cm^{-1} in the IR spectrum. Its ^1H NMR spectrum showed a doublet of doublets assigned to the proton under the hydroxyl at δ4.20 and a broad singlet at δ2.52 for the hydroxyl proton.

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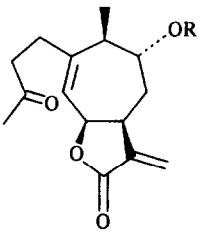

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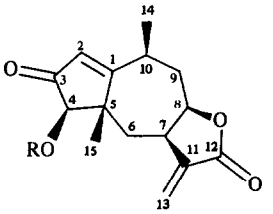

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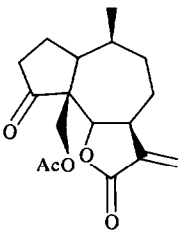

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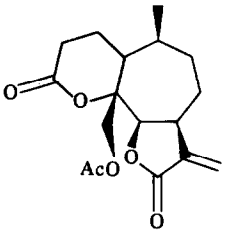

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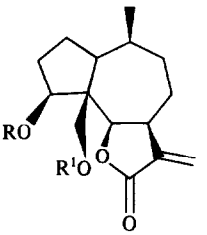
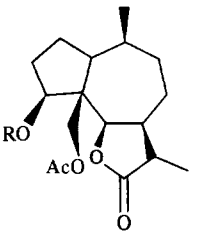


7 R = R¹ = Ac
8 R = H, R¹ = Ac
9 R = R¹ = H



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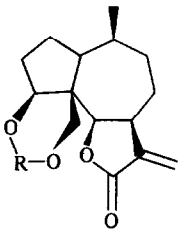
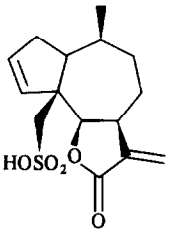
11 R = Ac



12 R = CMe_2
13 R = S=O



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Upon acetylation, compound **8** afforded ligulatine C (**7**) establishing the position of the secondary acetoxy group at C-4 in this compound. The tetrahydro-derivative **10** exhibited in its IR spectrum a hydroxyl band at 3580 cm^{-1} and in the ^1H NMR spectrum a doublet of doublets at δ4.15 (J = 9, 8 Hz) assigned to H-4. The new C-11 methyl group gave rise to the doublet at δ1.23 (J = 7 Hz). Upon acetylation **10** yielded the corresponding derivative (**11**) which was also obtained by sodium borohydride reduction of ligulatine C (**7**).

These correlations confirmed the structure **7** for ligulatine C and allowed us to infer the β-orientation of the hydroxyl at C-4, since the hydride enters by the less hindered α-face of the molecule. The easy preparation of the acetonide **12** and the cyclic sulphite **13** through the diol **9** obtained by hydrolysis of ligulatine C, proves this assumption. Both tetracyclic derivatives (**12** and **13**) exhibited a long range coupling (J = 2 Hz) between H-6 and H-15. The dehydrated derivative **14** was obtained as a minor product of the $SOCl_2$ treatment of **9**.

The new lactone 4-*O*-desacetyl ligulatine C was isolated from the more polar fractions of the extract. This compound was identical (mmp, TLC and spectral data) to the above mentioned dihydro derivative **8**. The new parthenolide, parthoximentine (**15**) was also isolated from this plant population. It exhibits IR bands for hydroxyl, saturated-γ-lactone and ester groups. Its ^1H NMR spectrum showed signals for tertiary and secondary methyl groups at δ1.20 *s* and δ1.23 *d*, respectively. The H-6 doublet at δ4.53 (J = 9 Hz) indicates a C-6 *cis*-lactone closure. The AB system (δ3.20 *d* and 3.11 *d*, J = 6 Hz) was assigned to the geminal protons at C-13 bearing the 11(13)-spiro epoxy group. The signal for the proton under the acetoxy group was located at δ5.25 (*ddd*, J = 7.5, 6.5, 3.5 Hz), while the proton under the hydroxyl group appeared as a triplet at δ3.99 (J = 9 Hz). Decoupling experiments established the sequence AcO–C(H)–CH_2–C(H)–OH where the central

Table 1. ^{1}H NMR spectral data of compounds **3** and **4** (80 MHz, $CDCl_3$, TMS as internal standard)

	3	3*	3†	3‡	3§	4
H-2	6.02 *s*	6.05 *s*	8.00	9.8	11.5	6.04 *s*
H-4	4.08 *s*	4.40 *s*	7.73	11.1	14.18	5.39 *s*
H-7	3.08‖ *m*	2.95‖ *m*	3.85			3.11‖ *m*
H-8	4.55 *ddd*	4.5 *ddd*	5.04	5.65		4.56 *ddd*
	11, 7.5, 4	11, 7.5, 4				11, 7.5, 4
H-13	6.29 *d*	6.24 *d*	6.51	6.81	7.3	6.29 *d*
	2.5	2.5				2.5
H-13′	5.63 *d*	5.37 *d*	5.81	6.02	6.29	5.67 *d*
	2	2				2
H-14	1.36 *d*	1.14 *d*	1.96	2.55	3.09	1.36 *d*
	7	7				7
H-15	1.26 *s*	1.38 *s*	3.38	4.43	5.87	1.26 *s*
OAc						2.24 *s*

*Run in pyridine-d_5.

†,‡,§Spectra after sequential addition of $Eu(fod)_3$. Mole ratios $[Eu(fod)_3/3]$ † = 0.19, ‡ = 0.41, § = 0.67.

‖Superimposed signal.

Table 2. ^{1}H NMR spectral data of compounds **6–14** (80 MHz, $CDCl_3$, TMS as internal standard)

	6	8	9	10	11	12	13	14
H-4		4.2*	4.34*	4.15 *dd*	5.19 *dd*	4.30*	4.6*	5.05 *m*
			9	9, 8	9, 8			
H-6	4.67 *d*	4.50 *d*	4.50 *d*	4.47 *d*	4.50 *d*	4.30 *dd*	4.35 *dd*	4.37 *d*
	9	9	9	9	8	8, 2	9, 2	9
H-7	3.45 *m*	3.37 *m*	3.40 *m*	2.84 *m*	2.75 *m*	3.37 *m*	3.40 *m*	3.46 *m*
H-13	6.25 *d*	6.15 *d*	6.20 *d*			6.24 *d*	6.25 *d*	6.27 *d*
	3	3.5	4	1.23 *d*	1.20 *d*	3.5	3.5	3.5
H-13′	5.50 *d*	5.45 *d*	5.47 *d*	7	7	5.43 *d*	5.50 *d*	5.49 *d*
	2.5	3	3.5			3.5	3.0	3.0
H-14	0.99 *d*	0.99 *d*	1.01 *d*	1.00 *d*	1.00 *d*	0.94 *d*	0.97 *d*	1.00 *d*
	8	7.5	7.5	7	7.5	7.5	7.5	7.5
H-15	4.35 *d*		4.07 *d*	4.49 *d*		3.80 *dd*	4.77 *dd*	
	12	4.25†	12	12	4.34†	12, 2	12, 2	4.15†
H-15′	4.07 *d*	(2H)	3.85 *d*	4.27 *d*	(2H)	3.56 *d*	3.95 *d*	(2H)
	12		12	12		12	12	
OAc	2.06 *s*	1.97 *s*		2.04 *s*				

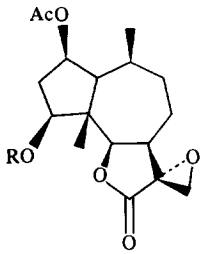
*Superimposed signal.

†Centre of an AB system.

methylene originated the *ddd* signals at δ2.70 and 1.58. In this manner, the acetoxy group was located at C-2 and the hydroxyl at C-4. This assumption was proved through the preparation of the acetyl derivative **16** and of the cyclopentanone **17**.

The chemical shift of the C-5 methyl group (δ1.20) and also the H-4 coupling constant values ($J_{3\alpha,4} = J_{3\beta,4}$ = 9 Hz) are indicative of the β-orientation of the C-4 hydroxyl in parthoximentine. When the hydroxyl group is α, the C-5 methyl group appears at higher field ($\sim \delta$0.85) and H-4 gives a doublet ($J \sim 5$ Hz) [9–13]. The H-2 coupling constants ($J_{1,2}$ = 6.5 Hz; $J_{2,3\alpha}$ = 3.5 Hz; $J_{2,3\beta}$ = 7.5 Hz) agree with an α-disposition of this proton. The stereochemistry at the remaining chiral centres C-1, C-5, C-6, C-7, C-10 and C-11 in parthoximentine was established by its conversion into the known stramonine B (**18**) [14].

The plant population collected in San Juan Guegoyache, Oaxaca, gave incanine (**5**), ligulatine C (**7**), 1-dehydroperuvinine (**3**) and a fourth lactone which was identified, by comparison with an authentical sample as parthomentine (**19**), a parthenolide previously isolated from this species collected in Tehuacán, Pue. [Romo de Vivar, A., personal communication]. From a fourth collection of this species, carried out in Teotitlán del Valle, Oaxaca, only 1-dehydroperuvinine (**3**) was isolated.



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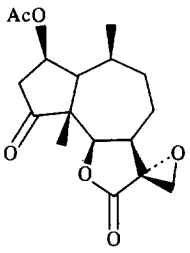
16 R = Ac



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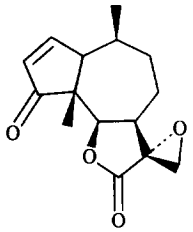

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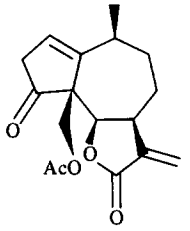

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Table 3. ^{1}H NMR spectral data of compounds **15**–**17** (80 MHz, $CDCl_3$, TMS as internal standard)

	15	**16**	**17**
H-2	5.25 *ddd* 7.5, 6.5, 3.5	5.24 *ddd* 8, 6, 3.5	5.49 *br t* 4.5
H-3α	1.58 *ddd* 15, 9, 3.5	*	*
H-3β	2.70 *ddd* 15, 9, 7.5	2.75 *ddd* 15, 9.5, 8.5	2.9*
H-4	3.99 *t* 9	5.10 *dd* 9.5, 8.5	
H-6	4.53 *d* 9	4.55 *d* 9.5	4.67 *d* 9
H-7	2.28 *m*	2.30 *m*	
H-13	3.20 *d* 6	3.19 *d* 6	3.22 *d* 6
H-13′	3.11 *d* 6	3.09 *d* 6	3.05 *d* 6
H-14	1.23 *d* 7	1.24 *d* 7	1.10 *d* 7
H-15	1.20 *s*	1.28 *s*	1.42 *s*
OAc	2.06	2.06 (6H)	2.06

*Superimposed signal.

EXPERIMENTAL

Four populations of *P. tomentosum* were analysed (voucher on deposit in the Herbarium of the Instituto de Biología, UNAM, MEXU). The first one was collected 13 km South of Teotitlán del Camino, Oaxaca. Dry leaves and flowers (1.5 kg) were extracted with $CHCl_3$ affording 101.6 g of residue, which was percolated through benthonitic earth ('Tonsil') with hexane, $CHCl_3$ and EtOAc yielding after solvent evaporation 31.7, 29.8 and 40.5 g of residue, respectively. The last two fractions were fractionated by CC (silica gel Merck 70–230 mesh). Fractions eluted with $CHCl_3$–Me_2CO (19:1) yielded 1.4 g of acetylivalbatine (**1**); fractions eluted with $CHCl_3$–Me_2CO (9:1) afforded 5 g of ivalbatine (**2**); elution with $CHCl_3$–Me_2CO (17:3) gave 90 mg of 1-dehydroperuvinine (**3**); mp 195–198°; UV λ_{max}^{EtOH} 224 nm (ε = 7866); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 1760, 1710, 1655; MS *m/z* (rel. int.): 262 $[M]^+$ ($C_{15}H_{18}O_4$), 247 $[M-Me]^+$, 244 $[M-H_2O]^+$, 229 $[M-Me-H_2O]^+$ 91 $[C_7H_7]^+$ (100). (Found: C, 68.68; H, 6.92; O, 24.40. Calc. for $C_{15}H_{18}O_4$: C, 68.52; H, 6.83; O, 24.40.)

The second population was collected in Mitla, Oaxaca. 1.78 kg of leaves and flowers were worked up as above yielding 157 g of extract. Four fractions were attained after percolation with hexane (41.5 g), $CHCl_3$ (53.2 g), EtOAc (34.4 g) and Me_2CO (10.7 g). The $CHCl_3$ fraction was chromatographed over silica gel (900 g) packed in $CHCl_3$. Fractions eluted with $CHCl_3$–Me_2CO (19:1) afforded a mixture of incanine (**5**) and ligulatine C (**7**) which were separated by repeated CC yielding 4.3 and 3.6 g of **5** and **7**, respectively.

Fractions eluted with $CHCl_3$–Me_2CO (9:1) yielded, after preparative TLC (Me_2CO–$CHCl_3$–hexane, 5:4:11, × 2) 30 mg of desacetyl ligulatine C (**8**), mp 134–138° (Me_2CO–hexane); UV λ_{max}^{EtOH} 220 nm (ε = 15 732); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3590, 1760, 1735, 1655; MS *m/z* (rel. int.): 248 $[M-AcOH]^+$, 233 $[248-Me]^+$, 230 $[248-H_2O]^+$, 215 $[230-Me]^+$. Mother liquors of fractions eluted with $CHCl_3$–Me_2CO (19:1, 9:1 and 17:3) crystallized yielding 240 mg of parthoximenthine (**15**), mp 183–186° (EtOAc–hexane); IR $\nu_{max}^{CHCl_3}$ cm^{-1}, 3540, 1785, 1730; MS *m/z*: 264 $[M-HOAc]^+$, 249 $[264-Me]^+$, 246 $[264-H_2O]^+$, 231 $[264-H_2O-Me]^+$.

A third population of this plant was collected in San Juan Guegoyache, Oax. The extract (152 g) obtained after extraction of leaves and flowers (1.725 kg) was worked up as above. Fractions eluted with $CHCl_3$–EtOAc (9:1) gave 2.3 g of **5** and 205 mg of parthomenthine (**19**), mp 166–169° (Me_2CO–hexane); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1740, 1660; ^{1}H NMR (80 MHz, $CDCl_3$, TMS as internal standard): δ 6.67 (*d*, 3.5 Hz, H-13), 5.55 (*d*, 3.5 Hz, H-13′), 6.05 (*t*, 2.5 Hz, H-2), 4.55 (*d*, 8.5 Hz, H-6), 4.34 (*s*, 2H); 2.97 (2H, H-3, H-3′), 1.10 (3H, H-14), 1.95 (3H, C-15 OAc).

The fourth population of *P. tomentosum* was collected in Teotitlán del Valle, Oaxaca. Extraction with $CHCl_3$ of 2.9 kg of leaves and flowers yielded 266 g of extract, which was worked up as above, affording, after CC (silica gel, $CHCl_3$–Me_2CO, 97:3), 127 mg of **3**.

Acetylation of ivalbatine (**2**). A soln of **2** (51 mg) in pyridine (0.5 ml) and Ac_2O (0.5 ml) was left to stand overnight and worked up as usual yielding 43 mg of acetyl ivalbatine (**1**).

Acetylation of 1-dehydroperuvinine (**3**). A soln of **3** (84 mg) in pyridine (1 ml) and Ac_2O (1 ml) was treated as above affording after preparative TLC ($CHCl_3$–Me_2CO, 4:1, × 2), 70 mg of **4**, mp 134–136° (Me_2CO–hexane): IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1735, 1720, 1660; EM *m/z* (rel. int.): 304 $[M]^+$ ($C_{17}H_{20}O_5$); 289 $[M-Me]^+$, 262 $[M-C_2H_2O]^+$, 247 $[M-C_2H_2O-Me]^+$, 244 $[M-HOAc]^+$, 216 $[M-HOAc-CO]^+$, 91 $[C_7H_7]^+$ (56), 43 [Ac] (100).

Baeyer–Villiger oxidation of incanine (**5**). A soln (5 ml) of HOOAc (2 ml), NaOAc (0.5 g) and H_2O (1.5 g) in HOAc were mixed with a soln of **5** (650 mg) in $CHCl_3$ (4 ml) and 10 ml of HOAc were added. The mixture was left in the darkness for 22 days. H_2O was added and the mixture was extracted with $CHCl_3$, washed with satd $NaHCO_3$ soln and H_2O, dried with anhydrous Na_2SO_4, and evaporated to dryness. Compound **6** (80.3 mg) was

obtained after CC purification (silica gel, $CHCl_3$), mp 185–186° ($CHCl_3$–hexane); IR ν_{max}^{KBr} cm^{-1}: 1760, 1730, 1715, 1640; CIMS *m/z*: 323 $[M+1]^+$ ($C_{17}H_{22}O_6$), 281 $[M+1-C_2H_2O]^+$, 262 $[M-HOAc]^+$, 249 $[M-C_2H_2O-MeO]^+$.

Reduction of incanine (**5**). $NaBH_4$ (150 mg) was slowly added to a cool (−20°) and stirred soln of **5** (303 mg) in MeOH (15 ml). The $NaBH_4$ excess was eliminated with HOAc. MeOH was evaporated *in vacuo* and the residue was extracted with $CHCl_3$, washed with satd $NaHCO_3$ soln, water, dried (Na_2SO_4) and evaporated to dryness. Two products were obtained after CC (silica gel; $CHCl_3$–Me_2CO, 9:1) of the residue (289 mg). The major product (**8**) (177 mg) crystallized from Me_2CO–*i*-Pr_2O, mp 134–138°; UV λ_{max}^{EtOH} 220 nm ($\varepsilon = 15732$); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3570, 1760, 1730, 1655. EIMS *m/z*: 248 $[M-HOAc]^+$, 233 $[M-HOAc-Me]^+$, 230 $[M-HOAc-H_2O]^+$; 215 $[M-HOAc-Me-H_2O]^+$. The minor component (**10**) (105 mg) crystallized from Me_2CO–hexane; mp 129–131°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 1765, 1730; EIMS *m/z*: 250 $[M-HOAc]^+$, 235 $[M-HOAc-Me]^+$, 232 $[M-HOAc-H_2O]$.

Acetylation of dihydroincanine (**8**). A soln of **8** (50 mg) in pyridine (1 ml) and Ac_2O (1 ml) was left to stand overnight at room temp. and worked up as usual. After crystallization 15 mg of ligulatine C (**7**) were obtained.

Acetylation of tetrahydroincanine (**10**). Compound **10** (50 mg) was treated as in the previous case. Crystallization from Me_2CO–hexane yielded 30.3 mg of **11**; mp 130–132°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1765, 1730; EIMS *m/z*: 292 $[M-HOAc]^+$, 232 $[M-2HOAc]^+$.

Reduction of ligulatine C (**7**). Compound **11** (39.6 mg) was prepared by the reduction of **7** (58 mg) following the same method as in the reduction of incanine.

Hydrolysis of ligulatine C (**7**). A suspension of **7** (115 mg) in 10% KOH (20 ml) was stirred at room temp. by 2 hr. After neutralization with 10% H_2SO_4, 10 ml of satd NaCl soln were added. The mixture was extracted with EtOAc, washed with H_2O, dried (Na_2SO_4) and evaporated to dryness to yield 90 mg of the diol **9**; colourless gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3430, 1745, 1630.

Acetonide **12**. A soln of **9** (90 mg) in dry Me_2CO (25 ml) containing *p*-toluensulphonic acid (15 mg) and molecular sieve (500 mg) was stirred at room temp. for 45 min then 5% $NaHSO_3$ soln was added and the solvent was evaporated *in vacuo*. The residue was extracted with EtOAc, washed with H_2O and dried (Na_2SO_4). Crystallization from EtOAc–hexane gave 20 mg of **12**; mp 137–139°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1655; EIMS *m/z* (rel. int.): 291 $[M-Me]^+$, 248 $[M-Me_2CO]^+$, 233 $[M-Me-Me_2CO]^+$, 204 $[M-Me_2CO-CO_2]^+$, 43 $[Ac]^+$ (100).

Sulphites **13** *and* **14**. $SOCl_2$ (0.3 ml) was slowly added to a cool (−20°) soln of **9** (89 mg) in pyridine (1 ml). The $SOCl_2$ excess was destroyed with H_2O. The mixture was extracted with $CHCl_3$, washed with 10% HCl, H_2O, dried and evaporated to dryness. The residue (two spots on TLC) was chromatographed on a silica gel column. Crystallization from $CHCl_3$–hexane gave compound **13**; mp 168–170°; IR ν_{max}^{mull} cm^{-1}: 1770, 1665, 1185 (SO_2), 700 (SO); EIMS *m/z*: 312 $[M]^+$ ($C_{15}H_{20}O_5S$); 248 $[M-SO_2]^+$, 230 $[M-SO_2-H_2O]^+$; 218 $[M-SO_2-CH_2O]^+$. The more polar component (**14**) is a gum; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3400, 1765, 1215 (SO_2); EIMS *m/z* $[M]^+$ ($C_{15}H_{20}O_5S$); 248 $[M-SO_2]^+$, 230 $[M-SO_2-H_2O]^+$; 218 $[M-SO_2-CH_2O]^+$.

Oxidation of parthoximentine (**15**). $(C_5H_5NH^+)_2Cr_2O_7^{2-}$ (2 g) [15] was added to a soln of **15** (40.7 mg) in CH_2Cl_2 (15 ml). The mixture was stirred overnight, diluted with hexane and percolated through a silica gel column. After solvent evaporation 30.7 mg of **17** were obtained. Liquid; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1790, 1743, 1710.

Stramonine B (**18**) *from parthoximentine* (**15**). A soln of **15** (40.8 mg) in Me_2CO (2 ml) was treated with Jones reagent at 4° until the persistence of an orange colour. The mixture was left at room temp. for 30 min, diluted with H_2O and extracted with EtOAc. The organic layer was washed with satd $NaHCO_3$ soln, H_2O and dried (Na_2SO_4). Crystallization from EtOAc–hexane gave 22.3 mg of stramonine B (**18**), mp 170–173° (lit. [5]: 175–176°).

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