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DITERPENES FROM *PALAFOXIA TEXANA*

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Key Word Index—*Palafoxia texana*; Compositae; rosene derivatives; diterpenes; 3β-acetoxy-jesromotetrol; 3β,19-diacetoxy-jesromotetrol.

Abstract—The investigation of *Palafoxia texana* afforded in addition to the known compound jesromotetrol two new rosene derivatives: 3β-acetoxy-jesromotetrol and 3β,19-diacetoxy-jesromotetrol. The structures were determined by spectroscopic methods and chemical transformations.

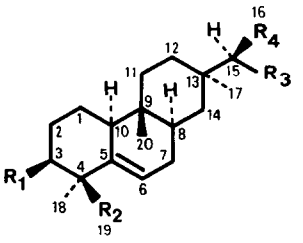
INTRODUCTION

Continuing our studies on the chemical components of the flora employed in Latin American folk medicine, we report here the results obtained in the study of *Palafoxia texana* D.C. (Compositae, Heleniae tribe) [1], gathered in Mexico, also known as *Polipteris texana* D.C.A. Gray, the botanical nomenclature of which is associated and discussed with the genus Othake [2, 3]. Bohlmann and Zdero [4], in a paper on the constituents of the roots of *P. texana*, reported the isolation of several sesquiterpenes derived from α-longipinene and α-bisabolol. Other species of the same genus have already been studied, such as *Palafoxia rosea* (Bush) by Bohlmann *et al.* [5] and Domínguez *et al.* [6, 7] and *P. arida* [8] by Herz *et al.* [9], who isolated new diterpenic compounds with different skeleta. In a latter work, Bohlmann and Zdero [10] revised the structures given as pimarane for several of the diterpenes isolated from *P. rosea*, to which they then assigned a rosane structure.

It is interesting to note that, although there exist noteworthy contributions to the literature on ^{1}H NMR of diterpenes having an isopimarane skeleton [11], or $\Delta^{8,14}$- and $\Delta^{8,9}$-pimarane skeletons [12, 13], as well as on ^{13}C NMR of $\Delta^{7,8}$- and $\Delta^{8,14}$-isopimaranes [14, 15], few outstanding studies have been carried out on the ^{13}C NMR of rosane diterpenes [16–18]. The ^{13}C NMR assignments for products **1** and **2** are given in Table 1.

RESULTS AND DISCUSSION

After successive chromatographies on silica gel of the ethanolic extract of the aerial part of *Palafoxia texana*, the following compounds were isolated. Compound **1**, $C_{24}H_{32}O_6$, mp 130–134°, $[\alpha]_D$ −68°, to which the structure 3β,19-diacetoxyjesromotetrol was assigned on the basis of the following considerations. Its IR spectrum showed bands of alcohol groups (3400 cm^{-1}) and esters (1715 and 1260 cm^{-1}). The ^{1}H NMR spectrum displayed signals at δ1.95 and 2.00 (3H, *s* each), two methyls of acetate groups, one of which is primary, δ4.27 and 4.05 (1H, *dd*, each J = 10 Hz), and another secondary, with a signal at δ4.90 (1H, *br s*). A signal at δ3.51 (1H, *t*) was assignable to the proton geminal to a secondary alcohol group. Further signals were at δ3.27 and 3.72 (1H, *dd*, each J = 10 Hz) for protons geminal to a primary alcohol group and at δ5.31 (1H, *br s*) for a vinylic proton. Signals



	R_1	R_2	R_3	R_4
1	OAc	CH_2OAc	OH	CH_2OH
2	OAc	CH_2OAc	OAc	CH_2OAc
3	OAc	CH_2OAc	O, CH_2, O	
4	OAc	CH_2OAc	=O	COOH
5	OAc	CH_2OAc	=O	$COOCH_3$
6	OAc	CH_2OH	OH	CH_2OH
7	OAc	CH_2OH	O, CH_2, O	
8	OH	CH_2OAc	O, CH_2, O	
9	OAc	COH	=O	COH
10	OH	CH_2OH	OH	CH_2OH
11	O, CH_2, O		O, CH_2, O	

Table 1. ^{13}C NMR chemical shifts of compounds 1 and 2

	1	2		1	2
C-1	19.2	21.4	C-11	33.7	32.5
C-2	25.1	27.2	C-12	29.2	31.2
C-3	73.1	75.3	C-13	36.7	38.8
C-4	41.8	43.8	C-14	36.3	36.0
C-5	139.8	141.9	C-15	79.4	75.3
C-6	119.5	121.7	C-16	63.3	64.8
C-7	30.3	31.3	C-17	18.6	20.6
C-8	35.6	37.7	C-18	24.6	26.7
C-9	34.9	37.1	C-19	68.7	70.9
C-10	46.0	48.1	C-20	12.3	14.5

corresponding to three angular methyls were also observed. Thus, compound **1** is a diterpene with two primary alcohol groups and two secondary, of which one primary group and one secondary group are acetylated. Acetylation of **1** in the usual manner afforded a tetraacetate whose physical and spectroscopic constants were superimposable with those given for jesromotetrol tetraacetate (**2**) [7]. Compound **1**, therefore, has a rosane skeleton. The relative positions of the acetate groups are yet unestablished. Treatment of **1** with copper sulphate in dry acetone afforded an acetonide **3** and, therefore, the free hydroxyl groups are both either on ring A or on the side chain of ring C. Oxidation of **1** with Jones reagent gave a ketoacid **4** which did not undergo decarboxylation even under the strongest conditions and which on treatment with diazomethane gave the ketomethylester **5**. Compound **4**, therefore, is not a β-ketoacid and the free hydroxyl groups must be situated on the side chain on ring C. The structure of **1**, a compound hitherto unreported in the chemical literature, was thus determined.

Compound **6**, a new compound, $C_{22}H_{30}O_5$, mp 212–214°C, $[\alpha]_D$ +29°, also displayed bands for alcohol and ester groups in its IR spectrum. The ^1H NMR spectrum showed signals for three angular methyls, the methyl of an acetate group at δ1.90 (3H, *s*) and its proton geminal at δ5.00 (1H, *m*), a signal at δ3.75 (5H, *m*) assignable to protons geminal to alcohol groups and a vinylic proton at δ5.50 (1H, *br s*). Acetylation of **6** afforded the jesromotetrol tetraacetate (physical and spectroscopical constants superposable with those of the compound obtained from **1**). Compound **6**, therefore, is a monoacetate of jesromotetrol. The position of the acetate is yet undetermined. Treatment of **6** with copper sulphate in dry acetone gave a mixture of two acetonides, **7** and **8**, which were separated by column chromatography. Compound **8** must be formed from **7** via a process of transacetylation. Separate acetylation of **7** and **8** led to the same acetonide diacetate **3**, identical with that obtained from **1**. The position of the acetate on ring A has yet to be defined. Treatment of **6** with pyridinium chlorochromate in dichloromethane afforded the dialdehyde **9**. The structure of **6** was thus assigned as the 3β-monoacetate of jesromotetrol.

From the most polar fraction, the tetrol **10** was obtained, the physical and spectroscopic constants of which, as well as those of its tetraacetate **2** and its diacetonide **11**, were superimposable with those given in the literature for jesromotetrol and its derivatives.

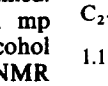
EXPERIMENTAL

Mps are uncorr. ^1H NMR were run on a 90 MHz and 200 MHz, ^{13}C NMR on a 50.3 MHz instrument in $CDCl_3$ with TMS as internal standard, IR in $CHCl_3$ and dry chromatography was performed on silica gel.

Isolation of the products. The methanolic extract (60 g) of the aerial part of *Palafoxia texana*, collected in Mexico (voucher specimen no. 7819 was deposited at the Department of Botany of the Instituto Tecnológico de Monterrey) was chromatographed over silica gel and eluted with petrol and petrol–EtOAc mixtures to yield several products:

3β,19-Diacetoxy jesromotetrol (**1**). Mp 130–134°, $[\alpha]_D$ −68° ($CHCl_3$; *c* 1.45). $[M]^+$ *m/z* 422.2617 (calc. for $C_{24}H_{32}O_6$, 422.2668). ^1H NMR (200 MHz): δ0.67, 0.89, 1.14 (3H, *s*, each, 3 Me), 1.95, 2.00 (3H, *s*, each, 2 AcO), 3.27, 3.72 (1H, *dd*, *J* = 10 Hz, each), 3.51 (1H, *t*), 4.27, 4.05 (1H, *dd*, *J* = 10 Hz, each), 4.90 (1H, *br s*), 5.31 (1H, *br s*). ^{13}C NMR (see Table 1). MS *m/z*: 422 $[M]^+$, 362, 349, 307, 302, 289, 287, 271, 253, 241, 227, 171, 159, 145, 131, 119 and 105. IR ν_{max} cm^{-1}: 3400, 2920, 1715, 1460, 1380, 1365, 1260, 1190, 1090, 1040, 1000, 950, 890 and 860.

Tetraacetoxy jesromotetrol (**2**). Compound **1** (100 mg) was acetylated in the usual way to yield 105 mg of **2**. Mp 152–154°, $[\alpha]_D$ −73° ($CHCl_3$; *c* 0.5) (lit. [7] 159°, $[\alpha]_D$ −85°). $[M]^+$ *m/z* 506.2883 (calc. for $C_{28}H_{42}O_8$, 506.2879). ^1H NMR (90 MHz, C_6D_6): δ0.63, 0.85, 1.07 (3H, *s*, each, 3 Me), 1.82 (6H, *s*, 2 AcO), 1.76, 1.73 (3H, *s*, each, 2 AcO), 4.01 (2H, *m*), 4.55 (2H, *m*), 5.16 (3H, *m*, $W_{\frac{1}{2}}$ = 16 Hz). ^1H NMR (200 MHz, $CDCl_3$): δ0.67, 0.97, 1.15 (3H, *s*, each, 3 Me), 1.96, 2.00, 2.01, 2.07 (3H, *s*, each, 4 AcO), 4.01 (1H, *d*, *J* = 10 Hz), 4.36, 4.42 (1H, *dd*, *J* = 10 Hz), 4.02, 4.28 (1H, *dd*, *J* = 10 Hz, each), 4.87, 4.91 (1H, *dd*, *J* = 10 Hz), 4.91 (1H, *t*), and 5.32 (1H, *br s*). ^{13}C NMR (see Table 1). MS *m/z*: 506 $[M]^+$, 446, 386, 326, 313, 271, 266, 253, 241 and 145. IR ν_{max} cm^{-1}: 2900, 1730, 1495, 1440 and 1370.

3β,19-Diacetoxy-15,16-acetonide of jesromotetrol (**3**). Compound **2** (80 mg) was dissolved in 10 ml of dry Me_2CO and treated with anhydrous $CuSO_4$ (80 mg) and refluxed for 2 hr; usual work-up yielded 75 mg of **3**. $[M]^+$ *m/z* 462.2964 (calc. for $C_{27}H_{42}O_6$, 462.2981). ^1H NMR (90 MHz, $CDCl_3$): δ0.70, 0.90, 1.17 (3H, *s*, each, 3 Me), 1.38, 1.40 (3H, *s*, each, 2 ), 1.99, 2.01 (3H, *s*, each, 2 AcO), 3.85 (3H, *m*), 4.02, 4.63 (1H, *d*, *J* = 14 Hz, each), 4.95 (1H, *t*), 5.37 (1H, *br s*). MS *m/z*: 462 $[M]^+$, 447, 402, 389, 342, 149. IR ν_{max} cm^{-1}: 2917, 1725, 1480, 1470, 1260, 1160, 1040 and 870.

15-Oxo-3β,19-diacetoxy-Δ^{8,14}-rosane-16-oic acid (**4**). A soln of 190 mg of **1** in Me_2CO (15 ml) was oxidized with Jones reagent, yielding 128 mg of **4**, mp 180–182°. ^1H NMR (90 MHz, $CDCl_3$): δ0.70, 1.19, 1.25 (3H, *s*, each, 3 Me), 1.98, 2.04 (2H, *s*, each, 2 AcO), 4.05, 4.35 (1H, *d*, *J* = 11 Hz, each), 4.95 (1H, *m*, $W_{\frac{1}{2}}$ = 8 Hz), 5.25 (1H, *m*, $W_{\frac{1}{2}}$ = 12 Hz). MS *m/z*: 406 $[M-CO]^+$, 346, 333, 286, 273, 245, 227, 149, 132, 119 and 105. IR ν_{max} cm^{-1}: 3400, 2800, 1725, 1700, 1470, 1440, 1370, 1255, 1190, 1150, 1130, 1100, 1040, 1000, 955, 900 and 800.

15-Oxo-3β,19-diacetoxy-Δ^{8,14}-rosane-16-oic acid methyl ester (**5**). A soln of 31.5 mg of **4** was methylated with CH_2N_2 to yield after chromatographic purification **5** (22 mg) as a gum which did not crystallize. ^1H NMR (60 MHz, $CDCl_3$): δ0.75, 1.19, 1.25 (3H, *s*, each, 3 Me), 1.98, 2.02 (3H, *s*, each, 2 AcO), 3.69 (3H, *s*, COOMe), 4.03, 4.37 (1H, *dd*, *J* = 10 Hz, each), 4.95 (1H, *m*, $W_{\frac{1}{2}}$ = 6 Hz), 5.40 (1H, *m*, $W_{\frac{1}{2}}$ = 6 Hz). MS *m/z*: 420 $[M-CO]^+$, 360, 347, 300, 287, 285, 245, 227, 145, 132, 119, 105, 95, 81, 55. IR ν_{max} cm^{-1}: 2910, 1720, 1470, 1430, 1380, 1370, 1260, 1190, 1090, 1040, 1000, 930 and 870.

3β-Acetoxy-jesromotetrol (**6**). Mp 212–214°, $[\alpha]_D$ +29° (C_5H_5N, *c* 0.1). $[M-H_2O]^+$ *m/z* 362.2455 (calc. for $C_{22}H_{34}O_4$,

362.2455). ^{1}H NMR (60 MHz, C_5D_5N): δ0.85, 1.07, 1.35 (3H, *s*, each, 3 Me), 1.90 (3H, *s*, AcO), 3.78 (5H, *m*), 5.00 (1H, *m*), 5.50 (1H, *m*). MS *m/z*: 362 $[M-H_2O]^+$, 349, 320, 289, 271, 259, 241, 229, 145. IR ν_{max}^{KBr} cm^{-1}: 3600–3200, 2910, 1705, 1460, 1440, 1260, 1180, 1160, 1100 and 890.

3β-Acetoxy-15,16-acetonide of jesromotetrol (**7**). Compound **6** (104 mg), dissolved in dry Me_2CO, was treated with anhydrous $CuSO_4$ as above, yielding after chromatographic purification two products, **7** (50 mg) and **8** (50 mg). Compound **7**: mp 158–160°, $[\alpha]_D$ −22° ($CHCl_3$, *c* 0.63). $[M-Me]^+$ *m/z*: 405.2642 (calc. for $C_{24}H_{37}O_5$, 405.2641). ^{1}H NMR (90 MHz): δ0.72, 0.91, 1.10 (3H, *s*, each, 3 Me), 1.34, 1.35 (3H, *s*, each ), 2.10 (3H, *s*, AcO), 3.75 (3H, *m*), 4.13, 4.98 (1H, *dd*, J = 10 Hz, each), 5.40 (1H, *br s*). MS *m/z*: 405 $[M-Me]^+$, 402 $[M-H_2O]^+$, 360, 330, 271, 258, 213, 145. IR ν_{max} cm^{-1}: 3490, 2915, 1725, 1450, 1380, 1370, 1250, 1155, 1040 and 1030.

19-Acetoxy-15,16-acetonide of jesromotetrol (**8**). Mp 120–122°, $[\alpha]_D$ −19° ($CHCl_3$, *c* 0.3). $[M-Me]^+$ *m/z*: 405.2632 (calc. for $C_{24}H_{37}O_5$, 405.2641). ^{1}H NMR (90 MHz): δ0.72, 0.91, 1.17 (3H, *s*, each, 3 Me), 1.36, 1.41 (3H, *s*, each, ), 2.06 (3H, *s*, AcO), 3.80 (4H, *m*), 4.00 (1H, *m*), 5.02 (1H, *br s*), 5.31 (1H, *br s*). MS *m/z*: 405 $[M-Me]^+$, 402 $[M-H_2O]^+$, 360, 330, 271, 258, 227, 145. IR ν_{max} cm^{-1}: 3500, 2915, 1720, 1450, 1380, 1370, 1250, 1150, 1038 and 860.

3β-Acetoxy-15-keto-16,19-dialdehyde of jesromotetrol (**9**). Compound **6** (105 mg), dissolved in CH_2Cl_2 (3 ml) was treated with a suspension of pyridinium chlorochromate (810 mg) in CH_2Cl_2 (6 ml) and stirred for 4 hr under an inert atmosphere to give, after work-up, the pure compound **9** as a gum which did not crystallize: ^{1}H NMR (90 MHz): δ0.82, 1.12, 1.27 (3H, *s*, each, 3 Me), 2.02 (3H, *s*, MeCOO), 4.91 (1H, *t*), 5.25 (1H, *t*), 9.41 (1H, *s*), 9.71 (1H, *s*). MS *m/z*: 331 $[M-Me-CO]^+$, 317, 275, 229, 215, 159, 145, 133, 119.

Jesromotetrol (**10**). Mp 185°. ^{1}H NMR (60 MHz, C_5D_5N): δ0.82, 1.09, 1.11 (3H, *s*, each, 3 Me), 3.70 (1H, *t*), 4.10, 4.10 (1H, *dd*, J = 6 Hz, each), 5.87 (2H, *br s*). MS *m/z*: $[M-H_2O]^+$, 290, 271, 258, 243, 229, 213, 199, 171, 159, 145.

Diacetonide of jesromotetrol (**11**). This was obtained as above. Mp 115–117°, $[\alpha]_D$ −18° ($CHCl_3$, *c* 0.35). ^{1}H NMR (90 MHz): δ0.70, 0.92, 1.22 (3H, *s*, each, 3 Me), 1.45 (12H, *s*, 2 ), 3.80 (6H, *m*), 5.17 (1H, *m*). MS *m/z*: 403 $[M-Me]^+$, 360, 302, 285, 258, 243, 225, 213, 199, 159, 119, 101. IR ν_{max} cm^{-1}: 2990, 2910, 1600, 1450, 1380, 1360, 1250, 1200, 1150, 1070, 1050, 1010, 870 and 860.

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