nology, which is sponsored by New York State Science and Technology Foundation. Generous support from Japan Halon Co. Ltd., Ajinomoto Co. Inc. and Fuji Chemical Ind. Ltd. is also gratefully acknowledged. I.O. is grateful to Dr. W. S, Knowles, Monsanto Co., for the generous gift of diPAMP and also to Dr. G. Prescher, Degussa A. G., for generously providing Degphos. We also thank Christine Hanson and Zhaoda Zhang for their technical assistance.

The Absolute Configuration of Jesromotetrol and Other *ent*-Rosenes

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The absolute configuration of jesromotetrol has been confirmed by the application of X-ray data published by other authors and the CD study of a derivative. The absolute configurations of three new products with rosene skeletons were established from spectral data, chemical transformations, and correlation with compounds with known absolute configurations.

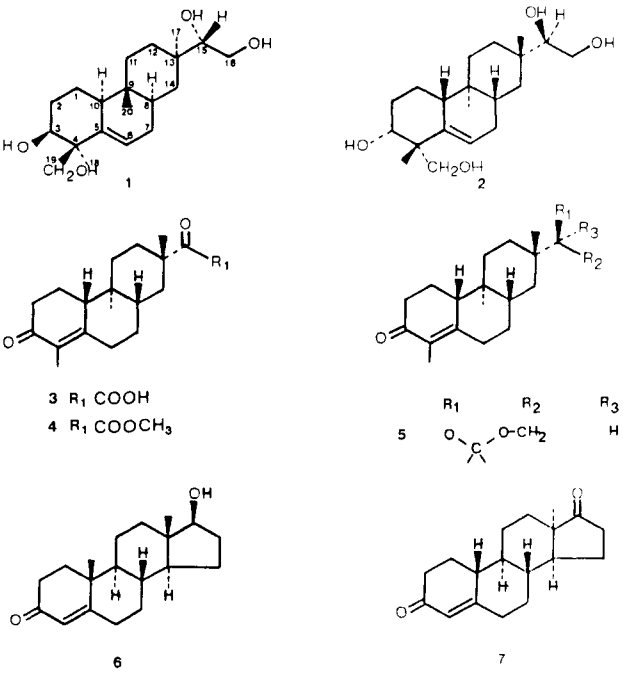
Introduction

Confusion abounds about diterpenes isolated from *Palafoxia*. For instance, Bohlmann et al.[1] first assigned a pimarane structure to some, later altering the identification to rosane,[2] and, later still, to *ent*-rosane,[3] arguing that the pimarane and rosane series can be clearly differentiated by their ^{13}C NMR data. They applied the same reasoning to other structures previously identified[4] as pimaranes. Elsewhere,[5,6] *ent*-isopimarene diterpenes have also been corrected to *ent*-rosenes.

In this paper a definitive sabsolute configuration is assigned to jesromotetrol[7,8] and related products isolated from various species of *Palafoxia*.

Earlier, the absolute configuration of jesromotetrol was given as **1**[7] although the X-ray diffraction data to support this assignment were not published at the time. The ^{13}C NMR data of jesromotetrol were analyzed[8] and were taken as confirming the structure. We ourselves reported[9] three new products that were correlated with **1**. However, the X-ray data for jesromotetrol, when published, only established its relative configurations.[10]

In view of the inconclusive nature of these data we decided to study jesromotetrol again in order to determine its absolute configuration. It was oxidized with Jones' reagent to yield a diketo acid **3**, from which methyl ester **4** was prepared, identified by its spectroscopic data (IR 3500–2880 cm^{-1}; UV 265 nm; no vinyl protons and a methyl on a conjugated double bond in ^1H NMR, 1.95 (d, J = 0.5, 3 H)). Compound **3** has an A, B, and C ring junction with an unsaturated α,β-ketone group in ring A, as do products **6** and **7**, earlier studied by circular dichroism[11-13] and which



were ideal for comparison purposes, with a negative Cotton effect at 340 nm and a positive one at around 250 nm, values similar to those shown by **3**. The absolute configuration of jesromotetrol was thus established as (3*R*,4*R*,8*S*,9*S*,10*R*,13*S*,15*R*)-3,15,16,18-tetrahydroxy-*ent*-ros-5-ene (**2**), enantiomeric to that previously assigned. All structures correlated with jesromotetrol[9] should be corrected accordingly.

Three products not previously reported were also isolated and were identified as 3-epijesromotetrol (**8**, (3*S*,4*R*,8*S*,9*S*,10*R*,13*S*,15*R*)-3,15,16,18-tetrahydroxy-*ent*-

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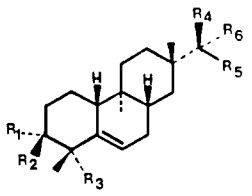
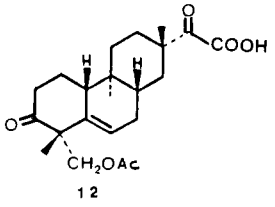
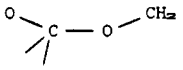
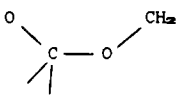
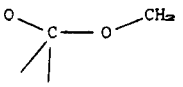
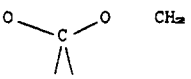
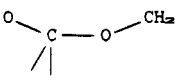
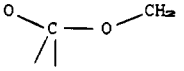
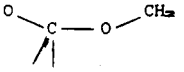
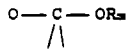
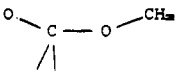
Chart I





12

	R_1	R_2	R_3	R_4	R_5	R_6
8	H	OH	CH_2OH	OH	CH_2OH	H
9	H	OAc	CH_2OH	OH	CH_2OH	H
10	H	OH	CH_2OAc	OH	CH_2OH	H
11	H	OAc	CH_2OAc	OAc	CH_2OAc	H
13	H	OAc	CH_2OH			H
14	H	OH	CH_2OAc			H
15	H	OAc	CH_2OAc			H
16	H					H
17	H	OH	CH_2OH			H
18	OH	H	CH_2OH			H
19	OAc	H	CH_2OAc	OH	CH_2OH	H
20	OAc	H	CH_2OAc	OAc	CH_2OAc	H
21		H				H

ros-5-ene) and **9** and **10**, two monoacetates of the same epimer series; when **8**, **9**, and **10** were acetylated with acetic anhydride and pyridine, they gave the same tetraacetate, **11** (Chart I). The ^1H and ^{13}C NMR data indicate that these compounds are related to jesromotetrol (**2**), which is confirmed by the oxidation of tetrol **8** with Jones' reagent, leading to the same diketo acid **3** with identical optical activity as the product obtained when jesromotetrol was oxidized. The absolute configurations of the chiral centers, C-8, C-9, C-10, and C-13 were established as *S*, *R*, *S*, and *S*, respectively, leaving the configuration of C-3, C-4, and C-15 to be determined. The hydroxymethylene group on C-4 in **8** is equatorial since a NOE difference experiment[14] shows H-6 and H-18 to be coplanar as in jesromotetrol (**2**), and so, the configuration at C-4 must be *R*. The stereochemistry of the C-3 was determined as *S* as the geminal proton of the hydroxy group at 3 is axial (^1H NMR). C-15 is part of a common 1-2 glycol system found in many natural products. There have been various unsuccessful attempts to determine the absolute configuration of C-15 in the *ent*-rosanes by simple ^1H and ^{13}C NMR methods.[15,16] Indirect correlation with jesromotetrol was applied by eliminating the C-3 configurational difference. Compound **5** was prepared by Cornforth's oxidation[17] from **9** as well as from **18**, whose absolute configuration is known. The products obtained show the same optical activity, and so C-15 in **8**, **9**, and **10** must be *R*. When **8** was treated with $CuSO_4$ and acetone, diacetonide **16** was formed.

Table I. ^{13}C NMR Data for 3, 10, 11, 16, 19, 20, and 21[a]

	3	10	11	16	19	20	21
C-1	21.3	23.16	22.6	18.8	19.7*	19.2	18.8
C-2	28.3	29.9	26.0	26.4	25.5*	25.1	26.4
C-3	196.0*	71.0	73.1	77.3	73.6	73.1	73.3
C-4	138.5	45.7	43.9	38.9	42.1	41.8	38.1
C-5	147.0	140.3	139.3	138.6	140.2	139.8	138.6
C-6	44.8	119.3	119.8	119.4	120.0	119.5	119.4
C-7	35.1	30.5	29.4	28.7	29.6	29.2	28.7
C-8	37.6	35.6	35.3	35.6	36.0	35.6	35.6
C-9	36.4	34.6	34.7	35.3	35.4	34.9	35.0
C-10	50.7	46.4	46.1	46.3	46.4	46.0	46.3
C-11	36.1	33.6	33.5	33.6	30.8	33.7	33.6
C-12	32.0	29.9	30.2	30.4	29.5	30.3	30.4
C-13	40.1	36.6	36.6	35.0	37.1	36.7	35.3
C-14	36.1	36.1	35.3	35.7	34.3	36.3	35.7
C-15	198.0*	81.1	79.1	84.7	73.6	79.4	84.7
C-16	184.0	62.6	63.1	64.5	63.1	63.3	64.5
C-17	19.7	18.4	18.7	18.4	18.9	18.6	18.4
C-18	-	68.3	64.5	66.5	69.2	68.8	66.5
C-19	11.5*	17.6	19.2	26.2	22.0	21.0	19.3
C-20	12.7*	12.3	12.3	11.9	12.8	12.3	11.9

[a] δ values are given from DEPT experiments. Values marked with an asterisk (*) within a column are interchangeable; the most probable values have been given.

A primary alcohol monoacetate, **10**, was oxidized with Jones' reagent to yield diketo acid **12**, which was identified by its spectroscopic data; **10** was consequently assigned the formula 18-acetoxy-(3*S*,4*R*,8*S*,9*S*,10*R*,13*S*,15*R*)-3,15,16-trihydroxy-*ent*-ros-5-ene. Both **9** and **10**, when treated with $CuSO_4$ in dry acetone, gave the same mixture of acetonides **13** and **14** via a trans-acetylation process already described,[9] and when this mixture was acetylated with acetic anhydride in pyridine, a single compound, **15**, was obtained. Compound **9** was accordingly assigned the formula (3*S*,4*R*,8*S*,9*S*,10*R*,13*S*,15*R*)-3-acetoxy-15,16,18-trihydroxy-*ent*-rosene. The ^{13}C NMR data shown in Table I agree with the structures proposed, and values have been assigned from DEPT experiments and correlation with literature data,[8] the values of the known natural products **19**, **20**, and **21** being given in the table for comparison purposes.

The mass spectral fragmentation pattern of the *ent*-ros-5-ene derivatives is in accordance with the structures proposed[18] as is that of the 18-norros-4-ene derivatives.[19]

Experimental Section

Melting points were determined on a Kofler-type apparatus and are uncorrected. ^1H NMR (200 MHz) and ^{13}C NMR (200 and 50 MHz) spectra were obtained on Bruker AC80 and WP-SY spectrometers, with $CDCl_3$ as solvent. High- and low-resolution MS were collected on a VG-Micromass spectrometer, Model ZAB-2F, at 15 or 70 eV. Optical activities were measured on a Perkin-Elmer 241 polarimeter. IR spectra were taken on a Perkin-Elmer Model 681 spectrometer using 0.1 mm sodium chloride cells, generally with $CHCl_3$ as solvent. UV spectra were obtained on a Perkin-Elmer 550SE instrument using 1 and 5 mm

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quartz cells and EtOH as solvent. CD curves were recorded on a Jobin-Yvon DIII CD apparatus.

A methanol extract (15 g) of the aerial part of *Palafoxia texana* D.C.A. Gray (Compositae) was chromatographed on Sephadex LH-20 and then rechromatographed on silica gel (60 PF 254) to give the following products in order of increasing polarity: **9** (10 mg); **10** (300 mg); **8** (1300 mg).

3,15-Dioxo-18-nor-*ent*-ros-4-ene-16-carboxylic Acid (3). Oxidation of **8** (30 mg, 0.09 mmol) with Jones' reagent using acetone as solvent and refluxing for 6 h yielded **3** (15 mg, 0.52 mmol, 52%) after usual workup. Oxidation of **2** under the same conditions also yielded **3**: mp 154–156 °C; $[\alpha]^{20}_D$ −18.2°; CD (MeCN) ϵ_{380} −1, ϵ_{270} +20; IR 3500, 2400, 2910, 1690, 1670, 1470, 1440, 1380, 1360, 1170, 1120 cm^{-1}; ^{1}H NMR δ 1.31 (s, 3 H), 1.95 (d, J = 0.5, 3 H), 2.35 (m, 5 H); MS m/z (rel intensity) 318 (M^+, 0.1), 304 (31), 290 (0.1), 276 (1), 258 (8), 243 (4), 230 (3), 215 (4), 152 (18), 136 (100); calcd mol wt for $C_{19}H_{26}O_4$ 318.1828, found mol wt 318.1874.

3,15-Dioxo-18-nor-*ent*-ros-4-ene-16-carboxylic Acid Methyl Ester (4). Esterification of **3** (11 mg, 0.034 mmol) with diazomethane yielded **4** (11 mg, 0.030 mmol, 88%): amorphous solid; UV λ_{max} (EtOH) 265, 203; IR 2940, 1730, 1450, 1380, 1370, 1240, 1130 cm^{-1}; ^{1}H NMR δ 0.90 (s, 3 H), 1.26 (s, 3 H), 1.95 (d, J = 0.5, 3 H), 3.70 (s, 3 H); MS m/z (rel intensity) 332 (M^+, 5), 318 (18), 291 (36), 287 (11), 257 (6), 243 (5), 231 (7), 182 (13), 136 (35), 107 (51), 105 (29), 95 (24), 59 (50); calcd mol wt for $C_{19}H_{26}O_4$ (M^+ − 14) 318.1817, found mol wt. 318.1824.

3β,15β,16,18-Tetrahydroxy-*ent*-ros-5-ene (8): mp 208–210 °C; $[\alpha]^{20}_D$ −12.2° (*c* 0.15, MeOH); IR (KBr) 3600–3000, 2900, 1450, 1380, 1350, 1075, 1050, 1020, 875 cm^{-1}; ^{1}H NMR δ 0.65 (s, 3 H), 0.92 (s, 3 H), 1.00 (s, 3 H), 3.33 (dd, J = 2.8, 9.3, 1 H), 3.54 (t, J = 9.3, 1 H), 3.77 (m, 4 H), 5.48 (br s, $W_{1/2}$ = 10, 1 H); MS m/z (rel intensity) 320 (M^+ − 18, 20.6), 289 (38.5), 271 (15.2), 253 (6.5), 243 (12.6), 229 (12.4), 159 (15.4), 145 (24.3), 131 (22.4), 119 (38.5), 105 (48.1); calcd mol wt for $C_{20}H_{32}O_3$ (M^+ − 18) 320.2280, found mol wt 320.2316.

3β-Acetoxy-15β,16,18-trihydroxy-*ent*-ros-5-ene (9): looked like transparent lacquer; IR 3600, 3450, 2910, 1720, 1470, 1380, 1370, 1250, 1090 cm^{-1}; ^{1}H NMR δ 0.67 (s, 3 H), 0.89 (s, 3 H), 0.91 (s, 3 H), 2.07 (s, 3 H), 3.25, 3.53, 3.72 (overlapping signals) (m, 5 H), 5.00 (dd, J = 5, 13, 1 H), 5.71 (br s, $W_{1/2}$ = 10, 1 H); MS m/z (rel intensity) 362 (M^+ − 18, 1), 320 (4), 302 (5), 287 (3), 253 (3), 213 (4), 171 (7), 121 (25), 105 (35), 95 (38); calcd mol wt for $C_{22}H_{34}O_4$ (M^+ − 18) 362.2259, found mol wt 362.2357.

18-Acetoxy-3β,15β,16-trihydroxy-*ent*-ros-5-ene (10): a white amorphous powder; mp 86–88 °C; IR 3600, 2910, 1720, 1380, 1370, 1250, 1090 cm^{-1}; ^{1}H NMR δ 0.64 (s, 3 H), 0.91 (s, 3 H), 0.94 (s, 3 H), 2.06 (s, 3 H), 3.31 (dd, J = 9.3, 2.6, 1 H), 3.39 (d, J = 4.2, 1 H), 3.45 (d, J = 4.2, 1 H), 3.53 (t, J = 9.3, 1 H), 3.72 (dd, J = 9.3, 2.6, 1 H), 5.56 (br s, $W_{1/2}$ = 10, 1 H); ^{13}C NMR (see Table); MS m/z (rel intensity) 362 (M^+ − H_2O, 6), 320 (11), 302 (37), 287 (22), 284 (6), 269 (19), 245 (11), 243 (15), 225 (16), 199 (13), 185 (16), 159 (24), 145 (37), 133 (29), 131 (29), 121 (43), 119 (48), 105 (52); calcd mol wt for $C_{20}H_{32}O_3$ (M^+ − 60) 320.2349, found mol wt 320.2359.

3β,15β,16,18-Tetraacetoxy-*ent*-ros-5-ene (11). Esterification of **9** (20 mg) with acetic anhydride in pyridine at room temperature for 24 h yielded **11** (18 mg): mp 158–160 °C: $[\alpha]_D^{20}$ +4.5° (*c* 1.5, $CHCl_3$); IR 3010, 2925, 1725, 1450, 1380, 1360, 1250, 1240, 910 cm^{-1}; ^{1}H NMR δ 0.63 (s, 3 H), 0.97 (s, 3 H), 0.99 (s, 3 H), 1.99 (s, 9 H), 2.07 (s, 3 H), 4.00 (dd, J = 2.3, 11.6, 1 H), 4.02 (br s, $W_{1/2}$ = 5.2, 2 H), 4.38 (dd, J = 2.3, 11.6, 1 H), 4.75 (dd, J = 4.5, 11.6, 1 H), 4.84 (dd, J = 2.3, 9.13, 1 H), 5.47 (br s, $W_{1/2}$ = 10, 1 H); MS m/z (rel intensity) 446 (M^+ − 60, 13.9) 386 (32.2), 371 (5.2), 326 (7), 311 (24.2), 266 (8.5), 253 (16.3), 251 (22.7), 145 (16.7), 132 (18.3), 131 (12.4), 119 (23.4), 105 (24.6); calcd mol wt for $C_{26}H_{38}O_6$ (M^+ − 60) 446.2622, found mol wt 446.2640.

3,15-Dioxo-18-acetoxy-*ent*-ros-5-ene-16-carboxylic Acid (12). Oxidation of **10** (30 mg, 0.08 mmol) with freshly prepared Jones' reagent yielded **12** (23 mg, 0.06 mmol, 74%): IR 3500, 2965, 1700, 1520, 1460, 1230, 1030 cm^{-1}; ^{1}H NMR δ 0.74 (s, 3 H), 1.20 (s, 3 H), 1.28 (s, 3 H), 1.97 (s, 3 H), 4.19 (d, J = 10.8, 1 H), 4.39 (d, J = 10.8, 1 H), 5.63 (br s, $W_{1/2}$ = 10, 1 H); MS m/z (rel intensity) 332 (M^+ − 58, 1), 316 (2), 304 (4), 290 (14), 275 (2), 241 (3), 225 (3), 181 (4), 107 (9), 105 (7), 95 (7).

3β-Acetoxy-18-hydroxy-*ent*-ros-5-ene 15β,16-Acetonide (13) and 18-Acetoxy-3β-hydroxy-*ent*-ros-5-ene 15β,16-Acetonide (14). The acetonides were formed by treating **10** (10 mg, 0.026 mmol) with anhydrous $CuSO_4$ (90 mg) and refluxing with dry acetone as solvent for 2 h. The isomers **13** and **14** were obtained in a 4:6 mixture (10 mg, 0.024 mmol, 90%). The mixture was not separated: ^{1}H NMR δ 0.65 (s, 3 H), 0.68 (s, 3 H), 0.89 (s, 3 H), 0.90 (s, 6 H), 0.99 (s, 3 H), 1.34 (s, 6 H), 1.40 (s, 6 H), 2.07 (s, 3 H), 2.08 (s, 3 H), 3.40 (dd, J = 4.5, 11.5, 1 H), 3.77 (m, 6 H), 4.07 (overlapping signals) (d, J = 11.5, 1 H), 4.47 (d, J = 11.5, 1 H), 5.57 (br s, $W_{1/2}$ = 10, 1 H), 5.72 (br s, $W_{1/2}$ = 10, 1 H).

3β,18-Diacetoxy-*ent*-ros-5-ene 15β,16-Acetonide (15). Ten milligrams of the 4:6 mixture **13** + **14** was acetylated with acetic anhydride and pyridine to give **15**: mp 152–154 °C: IR 2900, 1710, 1425, 1370, 1360, 1225, 1100 cm^{-1}; ^{1}H NMR δ 0.67 (s, 3 H), 0.90 (s, 3 H), 1.02 (s, 3 H), 1.35 (s, 3 H), 1.41 (s, 3 H), 2.02 (s, 3 H), 2.03 (s, 3 H), 3.76 (m, 2 H), 3.80 (t, J = 0.5, 1 H), 4.07 (d, J = 4, 2 H), 4.82 (dd, J = 4.6, 11.5, 1 H), 5.51 (br s, $W_{1/2}$ = 10, 1 H); MS m/z (rel intensity) 462 (M^+, 0.1), 447 (2), 402 (5), 360 (1), 342 (13), 327 (4), 284 (13), 271 (9), 171 (9), 119 (5), 105 (36), calcd mol wt for $C_{27}H_{42}O_6$ 462.2981, found mol wt 462.2991.

***ent*-Ros-5-ene 3β,18:15β,16-Diacetonide (16).** This biketal was prepared by dissolving tetrol **8** (86 mg, 0.25 mmol) in dry acetone, adding anhydrous $CuSO_4$ (200 mg), and then refluxing for 2 h. Compound **16** (85 mg, 0.20 mmol, 80%) was obtained: mp 215–217 °C; IR 2910, 1450, 1440, 1370, 1360, 1240, 1230, 1190, 1150, 1080, 1050, 1020, 850 cm^{-1}; ^{1}H NMR δ 0.64 (s, 3 H), 0.87 (s, 3 H), 1.17 (s, 3 H), 1.31 (s, 3 H), 1.37 (s, 3 H), 1.40 (s, 6 H), 3.54 (dd, J = 6, 8.8, 1 H), 3.72 (m, 3 H), 3.86 (d, J = 11.4, 2 H), 5.13 (br s, $W_{1/2}$ = 10, 1 H); MS m/z (rel intensity) 403 (M^+ − 15, 15), 360 (34), 258 (46), 243 (21), 213 (28), 145 (15), 138 (10), 133 (11), 130 (11), 120 (18), 119 (12), 118 (18), 109 (15), 108 (17), 107 (24), 105 (25), 101 (100), 95 (16), 79 (18).

3-Oxo-18-nor-*ent*-ros-4-ene 15β,16-Acetonide (5). Compound **18** (14 mg, 0.037 mmol), obtained from the mixture of **13** + **14** by hydrolysis, was oxidated with Cornforth's reagent for 12 h at room temperature and then refluxed for 2 h with acetone as solvent to give **5** (5 mg, 0.014 mmol, 40%): $[\alpha]^{20}_D$ −5° (*c* 0.02, $CHCl_3$); UV λ_{max} (EtOH) 227, 278, 285 nm; IR 2960, 1740, 1670, 1450, 1360, 1230, 1040 cm^{-1}; ^{1}H NMR δ 0.86 (s, 3 H), 0.93 (s, 3 H), 1.26 (s, 3 H), 1.35 (s, 3 H), 1.41 (s, 3 H), 1.95 (d, J = 2.5, 3 H), 2.36 (m, 4 H), 3.69 (d, J = 5, 1 H), 3.78 (s, 1 H), 3.88 (d, J = 5, 1 H); MS m/z (rel intensity) 346 (M^+, 1), 285 (1), 279 (6), 265 (2), 201 (2), 189 (1), 177 (2), 167 (18), 149 (100), 137 (6), 136 (6), 121 (5), 113 (4), 107 (6), 104 (7), 101 (26), 91 (7), 79 (12), 71 (14), 70 (11), 69 (11), 57 (36), 55 (31); calcd mol wt for $C_{22}H_{34}O_3$ (M^+) 346.2619, found mol wt 346.2609.

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