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# NORROSANE DERIVATIVES AND OTHER CONSTITUENTS FROM *HYMENOTHRIX WISLIZENII*

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**Key Word Index**—*Hymenothrix wislizenii*; Compositae; diterpenes; rosane derivatives; norditerpenes; borneol derivative; sesquiterpene lactones; guaianolides.

**Abstract**—The aerial parts of *Hymenothrix wislzenii* afforded, in addition to widespread compounds, a dihydroxy borneol triester, a new guaianolide, three rosane derivatives and two norditerpenes. The structures were elucidated by high field NMR techniques and the absolute configurations were determined by the CD curves of the norrosane derivatives. The structure of some diterpenes have been revised. The chemotaxonomy of the genus Hymenothrix and related ones is discussed.

## INTRODUCTION

Nothing is known about the chemistry of the small genus *Hymenothrix* (tribe Heliantheae) which is placed either in the subtribe Bahiinae [1] or in the subtribe Chaenactidinae [2] where the former is combined with elements of the *Chaenactis* group together with *Palafoxia*. To rectify this gap in our knowledge, we have investigated *Hymenothrix wislizenii*.

## RESULTS AND DISCUSSION

The extract of the aerial parts of *H. wislizenii* A. Gray afforded, in addition to widespread compounds (see Experimental), the borneol derivative **1**, the guaianolide **3** [3] and its corresponding diol **2**, the norditerpenes **4** and **5** as well as the rosane derivatives **6–9**.

In the mass spectrum of **1** the intensity of the molecular ion was too low for high resolution mass spectroscopy. The next peak (*m/z* 377), which was most likely formed by loss of an acetoxy residue, indicated a molecular formula $C_{24}H_{28}O_6$. This was confirmed by chemical ionization mass spectroscopy which gave the expected ion (*m/z* 437). In the $^1$H NMR spectrum all signals could be assigned by spin decoupling. The stereochemistry and the substitution pattern were determined by NOE difference spectroscopy which also showed that the benzoyloxy groups were at C-2 and C-8 of bornane while the acetoxy group had to be placed at C-5 when the chemical shifts were taken into account. The known esters of borneol clearly differ in the chemical shift of H-2 depending on the nature of the ester group. In a benzoate this proton is shifted by 0.15 ppm to lower fields when compared with the shift in the acetate. Furthermore, both H-9 and H-10 showed NOEs with the *ortho* protons of one of the benzoates and H-5 with both protons at C-8. These data established the relative positions of the ester groups.

The guaianolide **3** was identical with a lactone isolated previously from an *Eupatorium* species [3] and the $^1$H NMR spectrum of **2** (see Experimental) was very close to that of **3**. As in similar cases characteristic shift differences, especially for H-8 and H-13′, were observed.

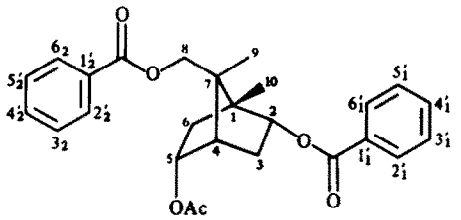
The norditerpene **4** was identical with norjulslimdiolone [4] which was obtained by oxidation of julslimtetrol [4]. Spin decoupling and also the fragmentation pattern, which resembled that of corresponding steroids [5], clearly showed that norrosane derivatives were present. As shown in the Scheme, splitting of the 9,10-bond in **4** and **5** and transfer of H-8 to C-10 led to **5a** which in a cyclic mechanism gives **5b**. The observed NOEs of **4** and **5** (Table 1) showed that both were present in the steroid conformation. Accordingly, the absolute configuration followed from the observed Cotton-effect. As in similar steroids [6] the n-$\pi^*$-band has a negative and the $\pi$-$\pi^*$-band a positive sign. Furthermore, the optical rotation of the julslimdiolone isolated together with jesromotetrol from *Palafoxia rosea* [7], its structure being established by X-ray analysis [8], had the same sign. Therefore the absolute configuration of all rosane derivatives from *Palafoxia* should be the same [7–9].

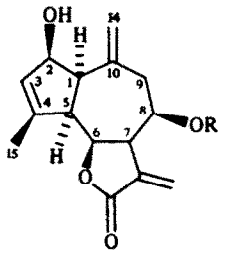
The stereochemistry at C-6 in the ketone **5**, which on acetylation gave a triacetate, followed from the observed couplings (Table 1) and the absence of a NOE between H-10 and H-6. Furthermore, the 6$\beta$-hydroxy group led to a pronounced down field shift of H-10$\beta$. The $^{13}$C NMR spectra of **4** and **5Ac** (Table 2) also supported the proposed structures and configurations.

The spectral data and also the optical rotation of **6** were identical with those of julslimtetrol [4]. As this tetrol was converted to **4** [4] julslimtetrol also is a rosane derivative.

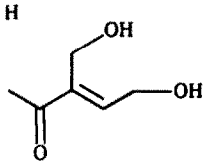
The $^1$H NMR spectrum of **7** (Table 3) was close to that of **6**. The altered chemical shifts, especially of H-18 and H-19 showed that these compounds were isomeric at C-4. While in the case of **6Ac** irradiation of the 4-methyl group gave NOEs with H-6 (12%) and H-3 (8%), both methylene protons (H-18) in **7** showed a NOE with H-6 (5%).

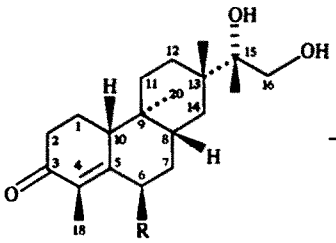
Compounds **8** and **9** were purified as their triacetates **8Ac** and **9Ac**. The $^1$H NMR spectra (Table 3) indicated that these diterpenes differed from **6** and **7** by the absence

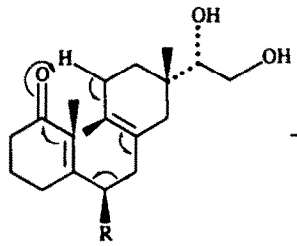


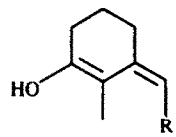


2 R = H

3 R = 





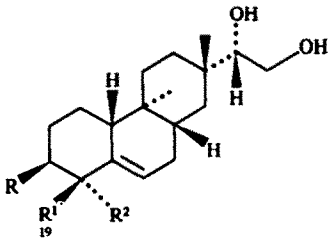


| | 4 | 5 | 5Ac |
|---|---|---|---|
| R | H | OH | OAc |

5a

5b

*m/z* 124.14



| | R | $R^1$ | $R^2$ |
|---|---|---|---|
| 6 | OH | $CH_2OH$ | Me |
| 7 | OH | Me | $CH_2OH$ |
| 8 | OH | $CH_2OH$ | Me |
| 9 | OH | Me | $CH_2OH$ |

of an oxygen function at C-3. All data indicated again the presence of isomers at C-4. As in the case of 7, 9 Ac showed clear NOEs between H-6 and both protons at C-18 (6%). As followed from models, this requires an α-hydroxymethylene group. The $^{13}C$ NMR spectrum of **9***Ac* (Table 2) also agreed with the proposed structure. Characteristic is the chemical shift of C-20 which differs clearly from the corresponding signal in pimaranes [10].

The isolation of **4–9** from this *Hymenothrix* species strongly supports the placement of *Palafoxia* in the same subtribe. Guaianolides close to **2** and **3** have been reported from *Bahia* and *Picradeniopsis* [11, 12], both placed in the same subtribe. More difficult are the chemical relationships to further genera of the subtribe Chaenactidinae where many genera which were previously members of the tribe *Helenieae* have been placed. From *Chaenactis* [13] and *Schkuhria* [14] the isolation of eupatoriopicrin has been reported. As this lactone most likely is the precursor of the guaianolide 3 this could be an indication of a relationship. No relationships, however, are visible to the chemistry of *Arnica*, where pseudoguianolides are widespread. However, the placement of *Palafoxia* in the tribe Eupatorieae has been discussed [15]. As rosane derivatives and similar guaianolides are present in *Trichogonia* [16] further investigations are necessary to get a clear picture of the chemotaxonomy of these genera.

## EXPERIMENTAL

$^1$H NMR: 400 MHz, $CDCl_3$, TMS as int. standard; MS: 70 eV direct inlet; $^{13}$C NMR: 50.32 MHz, $CDCl_3$. CC: silica gel (70–230 mesh, Merck); PTLC and TLC: silica gel (Pf 254, Merck); HPLC: RP8 columns, 3 ml/min, *ca* 100 bar.

The air dried aerial parts (900 g, collected near Monterrey, Mexico, voucher 8031, deposited in the Herbarium of I.T.E.S.M.,

Table 1. $^1$H NMR spectral data of compounds **4**, **5** and **5Ac** (400 MHz, $CDCl_3$, TMS as int. standard)

| H | 4 | 5* | 5Ac† |
|---|---|---|---|
| 1α | 1.66 *dddd* | 1.64 *dddd* | 1.71 *dddd* |
| 1β | 2.00 *dddd* | 2.00 *dddd* | 2.02 *m* |
| 2α | 2.43 *ddd* | 2.40 *ddd* | 2.45 *ddd* |
| 2β | 2.19 *ddd* | 2.21 *ddd* | 2.26 *ddd* |
| 6α | 2.87 *ddd* | 4.79 *dd* | 5.94 *dd* |
| 6β | 2.03 *m* | — | — |
| 10 | 2.03 *br d* | 2.51 *br d* | 2.42 *m* |
| 15 | 3.31 *dd* | 3.21 *dd* | 4.89 *dd* |
| 16 | 3.74 *dd* | 3.64 *dd* | 4.40 *dd* |
| 16′ | 3.52 *dd* | 3.41 *dd* | 4.00 *dd* |
| 17 | 0.94 *s* | 0.90 *s* | 1.07 *s* |
| 18 | 1.77 *dd* | 1.79 *d* | 1.85 *d* |
| 20 | 0.64 *s* | 0.58 *s* | 0.64 *s* |

*$CDCl_3/CD_3OD$ (5:1).

†OAc: 2.07 *s*; 2.04 *s*; 2.00 *s*.

*J*[Hz]: 1α,1β = 1α,2β = 14; 1α,2α = 1β,2β = 13,10 = 4; 1α,10 = 10; 1β,2α = 5; 2α,2β = 15; 15,16 = 2.5; 15,15′ = 9; 16,16′ = 11.5; compound **4**: 6α,6β = 16; 6α,7α = 1.5; 6α,7β = 4.5; 6β,18 = 10,18 = 1.5; compounds **5** and **5Ac**: 6,7α = 6,7β = 3; 10,18 = 2. NOEs for **4** and **5**: Irradiation of H-10 → H-8β (8%), H-2β (3%)*m* H-11β (4%) of H-17 → H-8β (10%), H-11β (6%), H-15 (3%), H-16 (2%), H-16′ (3%); of H-20 → H-1α (6%) H-7α (8%), H-14α (7%).

Table 2. $^{13}$C NMR spectral data of compounds **4**, **5Ac**, **6Ac** and **9Ac** (67.9 MHz, $CDCl_3$)

| C | 4 | 5Ac | 6Ac | 9Ac |
|---|---|---|---|---|
| 1 | 20.5 *t* | 20.3 *t* | 22.5 *t* | 25.7 *t* |
| 2 | 36.8 *t* | 36.4 *t* | 26.6 *t* | 21.0 *t* |
| 3 | 199.6 *s* | 199.9 *s* | 78.0 *d* | 34.8 *t* |
| 4 | 131.0 *s* | 135.0 *s* | 44.3 *s* | 39.0 *s* |
| 5 | 157.9 *s* | 150.4 *s* | 138.2 *s* | 141.4 *s* |
| 6 | 30.7 *t* | 68.8 *d* | 123.3 *d* | 117.4 *d* |
| 7 | 28.2 *t* | 32.9 *t* | 29.3 *t* | 29.5 *t* |
| 8 | 39.4 *d* | 33.6 *d* | 34.7 *d* | 35.4 *d* |
| 9 | 38.4 *s* | 38.4 *s* | 34.6 *s* | 34.7 *s* |
| 10 | 50.4 *d* | 46.4 *d* | 46.1 *d* | 36.9 *d* |
| 11 | 33.3 *t* | 33.6 *t* | 33.3 *t* | 33.5 *t* |
| 12 | 29.4 *t* | 29.4 *t* | 30.3 *t* | 30.1 *t* |
| 13 | 36.4 *s* | 36.5 *s* | 36.5 *s* | 36.5 *s* |
| 14 | 35.9 *t* | 35.1 *t* | 35.2 *t* | 35.4 *t* |
| 15 | 81.0 *d* | 78.1 *d* | 79.1 *d* | 79.2 *d* |
| 16 | 62.5 *t* | 62.9 *t* | 63.0 *t* | 63.1 *t* |
| 17 | 18.6 *q* | 18.9 *q* | 18.5 *q* | 18.6 *q* |
| 18 | 11.0 *q* | 11.0 *q* | 19.6 *q* | 71.8 *t* |
| 19 | — | — | 65.4 *t* | 24.8 *q* |
| 20 | 12.8 *q* | 12.3 *q* | 12.1 *q* | 12.2 *q* |
| OAc | — | 20.8 *q* | 20.8 *q* | 20.8 *q* |
| | | 20.9 *q* | 20.9 *q* | 21.0 *q* |
| | | 21.3 *q* | 20.9 *q* | 21.0 *q* |
| | | 169.7 *s* | 21.1 *q* | 170.8 *s* |
| | | 170.6 *s* | 170.3 *s* | 171.0 *s* |
| | | 170.9 *s* | 170.6 *s* | 171.4 *s* |
| | | | 170.7 *s* | |
| | | | 170.9 *s* | |

Multiplicity estimated by DEPT spectra.

Table 3. $^1$H NMR spectral data of compounds **6**, **6Ac**, **7**, **8Ac** and **9Ac** (400 MHz, $CDCl_3$, TMS as int. standard)

| H | 6* | 6Ac | 7* | 8Ac | 9Ac |
|---|---|---|---|---|---|
| 3 | 3.24 *dd* | 4.60 *dd* | 3.65 *dd* | † | † |
| 6 | 5.59 *br d* | 5.58 *br d* | 5.41 *br ddd* | 5.51 *br ddd* | 5.36 *br ddd* |
| 10 | 1.72 *m* | 1.94 *br d* | 1.84 *br d* | 1.92 *br d* | 1.89 *br d* |
| 15 | 3.16 *dd* | 4.87 *dd* | 3.24 *dd* | 4.82 *dd* | 4.90 *dd* |
| 16 | 3.52 *dd* | 4.38 *dd* | 3.67 *dd* | 4.15 *m* | 4.41 *dd* |
| 16′ | 3.27 *dd* | 3.99 *dd* | 3.44 *dd* | | 4.02 *dd* |
| 17 | 0.80 *s* | 0.97 *s* | 0.87 *s* | 0.96 *s* | 0.99 *s* |
| 18 | 1.22 *s* | 1.07 *s* | 3.78 *d*<br>3.71 *d* | 1.03 *s* | 4.13 *d*<br>3.98 *d* |
| 19 | 3.97 *d*<br>3.14 *d* | 4.52 *d*<br>3.85 *d* | 0.97 *s* | 4.11 *d*<br>4.04 *d* | 1.04 *s* |
| 20 | 0.54 *s* | 0.62 *s* | 0.62 *s* | 0.66 *s* | 0.64 *s* |
| OAc | — | 2.07 *s* | — | 2.04 *s* | 2.09 *s* |
| | | 2.03 *s* | | 2.03 *s* | 2.05 *s* |
| | | 1.99 *s* | | 2.02 *s* | 2.02 *s* |
| | | 1.97 *s* | | | |

*$CDCl_3/CD_3OD$(5:1).

†Obscured multiplets.

*J*[Hz]: 1α,10 = 11; 6,7 = 5; 6,7′ = 3; 6,10 = 1.5; 15, 16 = 2.5; 15,16′ = 9; 16,16′ = 11.5; 18,18′ = 19,19′ = 11; compounds **6**, **6Ac** and **7**: 2α,3 = 4; 2β,3 = 12.

Monterrey) was extracted with MeOH–petrol–isopropyl ether (1:1:1) at room temp. The extract obtained was defatted by treatment with MeOH and separated as reported previously [17] into three fractions [1:petrol and petrol–$Et_2O$(9:1); 2: $Et_2O$–petrol(1:1) and 3: $Et_2O$–MeOH(9:1)]. PTLC of fraction 1 gave 130 mg caryophyllene and 100 mg germacrene D. PTLC of fraction 2 ($Et_2O$–petrol, 1:4, three developments) gave 10 mg spathulenol and 50 mg **1** ($R_f$ 0.25). HPLC (RP 8, MeOH–$H_2O$, 7:3, *ca* 100 bar) of one fifth of fraction **3** gave four crude fractions (3/1: $R_t$ 1.6 min.; 3/2: $R_t$ 3.0 min.; 3/3: $R_t$ 4.0 min. and 3/4: $R_t$ 7.2 min.). PTLC of 3/1 (EtOAc, three developments) gave 20 mg **2** ($R_f$ 0.45), 20 mg **3** ($R_f$ 0.39) and 40 mg **5** ($R_f$ 0.27). Fraction 3/2 could be separated only after acetylation ($Ac_2O$, 2 hr, 70°). PTLC (toluene–$CH_2Cl_2$–$Et_2O$, 9:9:2, two developments) gave 5 mg **9**Ac ($R_f$ 0.35) and 3 mg **8**Ac ($R_f$ 0.26). PTLC of 3/3 (EtOAc) gave 10 mg **7** ($R_f$ 0.21) and 100 mg **6** ($R_f$ 0.18) while PTLC (EtOAc) of 3/4 gave 12 mg **4** ($R_f$ 0.30). Known compounds were identified by comparing the 400 MHz $^1$H NMR spectra with those of authentic material.

2α,8-*Dibenzoyloxy-5α-acetoxybornane* (**1**). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1745 (OAc), $PhCO_2R$ (1730); MS *m/z* (rel. int.): 436 $[M]^+$ (0.5), 377.175 $[M-OAc]^+$ (2.5) (calc. for $C_{24}H_{25}O_4$: 377.175), 315 $[M-OCOPh]^+$ (8), 105 $[PhCO]^+$ (100); CIMS *m/z* (rel. int.): 437 $[M+1]^+$ (7), 315 $[437-PhCO_2H]^+$ (100), 255 $[315-HOAc]^+$ (8); $^1$H NMR ($CDCl_3$): δ5.02 (*ddd*, H-2, *J* = 10, 3.5, 1.5 Hz), 1.93 (*dd*, H-3, *J* = 14.5, 3.5), 2.34 (*dddd*, H-3β, *J* = 14.5, 10, 4, 1), 2.53 (*dd*, H-4, *J* = 4, 4), 5.46 (*br ddd*, H-5, *J* = 9, 4.5, 4), 2.20 (*dd*, H-6, *J* = 15, 4.5), 2.14 (*ddd*, H-6β, *J* = 16, 9, 1), 4.44 and 4.33 (*d*, H-8, *J* = 11.5), 1.21 (*s*, H-9), 1.00 (*s*, H-10); OCOR: 8.06 and 8.02 (*d*, H-21, H-22, *J* = 8), 7.46 (*dd*, H-31, H-32, *J* = 8, 8), 7.57 (*dd*, H-41, H-42), 2.08 (*s*, OAc); $[\alpha]_D^{24°}$ + 10 ($CHCl_3$; *c* 0.72).

2β,8β-*Dihydroxyguaia*-3,10(14),11(13)-*trien*-12,6α-*olide* (**2**). Colourless oil; IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3600 (OH), 1770 (γ-lactone); MS *m/z* (rel. int.): 262 $[M]^+$ (3), 244.110 $[M-H_2O]^+$ (13) (calc. for $C_{15}H_{16}O_3$: 244.110), 232 $[M-CH_2O]^+$ (24), 161 (100), 91 (64); $^1$H NMR ($CDCl_3$): δ3.09 (*dd*, H-1, *J* = 8.5, 6.5 Hz), 4.64 (*br d*, H-2, *J* = 6.5), 2.60 (*br dd*, H-5, *J* = 10.5, 8.5), 4.53 (*dd*, H-6, *J* = 10.5, 8.5), 2.98 (*dddd*, H-7, *J* = 8.5, 4, 3.5, 3), 4.22 (*ddd*, H-8, *J* = 7.5, 7, 4), 2.76 (*dd*, H-9, *J* = 13.5, 7), 2.59 (*dd*, H-9′, *J* = 13.5, 7.5), 6.38 (*d*, H-13, *J* = 3.5), 5.59 (*d*, H-13′, *J* = 3), 5.08 and 5.03 (*br s*, H-14), 1.94 (*br s*, H-15).

*Julslimdiolone* (**4**). CD (MeCN): $\Delta\varepsilon_{314} - 2.8$; $\Delta\varepsilon_{250} + 70$; MS *m/z* (rel. int.): 306.219 $[M]^+$ (20) (calc. for $C_{19}H_{30}O_3$: 306.219), 245 $[M-CH(OH)CH_2OH]^+$ (7), 124 [**5***b*]$^+$ (100).

6β-*Hydroxyjulslimdiolone* (**5**). Colourless oil; MS *m/z* (rel. int.): 322.214 $[M]^+$ (12) (calc. for $C_{19}H_{30}O_4$: 322.214), 304 $[M-H_2O]^+$ (19), 243 $[304-CH(OH)CH_2OH]^+$ (37), 140 [**5***b*]$^+$ (100). Acetylation ($Ac_2O$, 2 hr, 70°) gave **5**Ac; colourless oil; IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1755, 1250 (OAc), 1690 (C=CC=O); MS *m/z* (rel. int.): 388.225 $[M-HOAc]^+$ (4) (calc. for $C_{23}H_{32}O_5$: 388.225), 328 $[388-HOAc]^+$ (4), 268 $[328-HOAc]^+$ (5), 61 $[AcOH_2]^+$ (100).

4-epi-*Julslimtetrol* (**7**). Colourless oil; MS *m/z* (rel. int.): 320. 235 $[M-H_2O]^+$ (18) (calc. for $C_{20}H_{32}O_3$: 320.235); 302 $[320-H_2O]^+$ (3), 289 $[320-CH_2OH]^+$ (22), 271 $[289-H_2O]^+$ (8), 60 $[OCHCH_2OH]^+$ (100).

3-*Desoxyjulslimtetrol triacetate* (**8***Ac*). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1750, 1260 (OAc); MS *m/z* (rel. int.): 448 $[M]^+$ (2), 388.261 $[M-HOAc]^+$ (28) (calc. for $C_{24}H_{36}O_4$: 388.261), 375 $[M-CH_2OAc]^+$ (24), 328 $[388-HOAc]^+$ (68), 313 $[328-Me]^+$ (28), 253 $[313-HOAc]^+$ (24), 145 $[CH(OAc)CH_2OAc]^+$ (62), 55 (100).

3-*Desoxy-4-epi-julslimtetrol triacetate* (**9***Ac*). Colourless oil; IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1740, 1240 (OAc); MS *m/z* (rel. int.): 448. 282 $[M]^+$ (4) (calc. for $C_{26}H_{40}O_6$: 448.282), 388 $[M-HOAc]^+$ (21), 375 $[M-CH_2OAc]^+$ (70), 328 (12), 315 (31), 255 (100), 253 (22).

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