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SHORT REPORTS

GUAIANOLIDES FROM *GOCHNATIA SMITHII**

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Key Word Index—*Gochnatia smithii*, Compositae, sesquiterpene lactones, guaianolides, 8α-acetoxydehydrocostus lactone, 8α-tigloyloxydehydrocostus lactone

Abstract—The structure and stereochemistry of 8α-acetoxy and 8α-tigloyloxy dehydrocostus lactones, two guaianolides isolated from the aerial parts of *Gochnatia smithii*, were established by chemical and spectroscopic methods

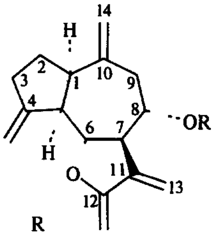
INTRODUCTION

From the large genus *Gochnatia* (tribe Mutisieae, Compositae) only five species have been analyzed chemically [1–4] Although all of them contain triterpenes, sesquiterpene lactones have been found only in *G discoidea* [2], *G rusbyana* [3] and *G paniculata* [4] From the last two zaluzanin C and dimeric guaianolides were also isolated We now report the isolation of two guaianolides from *Gochnatia smithii* Robins & Greemm, both of them closely related to dehydrocostus lactone derivatives isolated from Vernonieae tribe [5, 6]

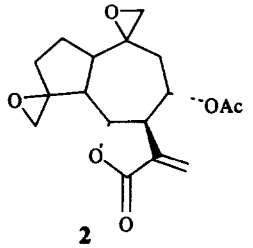
DISCUSSION

The major component, compound A, $C_{17}H_{20}O_4$ (MS), mp 120–121°, $[\alpha]_D$ + 87 3° (*c* 0 179, $CHCl_3$), is a sesquiterpene lactone of the guaianolide type and it was formulated as **1a** This compound showed absorption bands in the IR spectrum at 1768 cm^{-1} (γ-lactone-α,β-unsaturated), 1735 cm^{-1} (saturated ester), 1653 and 1640 cm^{-1} (double bonds) The ^1H NMR spectrum revealed the presence of three terminal methylenes, one of them corresponding to that conjugated with the γ-lactone (δ6 18, *d*, J = 3 5 Hz and 5 61, *d*, J = 3 Hz) The other two methylenes were located at C-14 (5 01, *s br* and 4 89 *s br*) and C-15 (5 24, *s br* and 5 06, *s br*) The signal for the proton under the lactone oxygen bridge appeared as a doublet of doublets at 3 98 (J = 10, 9 Hz), its multiplicity and coupling constants in agreement with a *trans*-γ-lactone closed to C-6 At higher field one singlet for an acetate methyl group was evident (2 11, *s*, 3H) Although the signal for the proton under this group was overlapped with the signals of the terminal methylene protons, this functionality was tentatively located at C-8 In order to sweep out the methylene signals compound A (**1a**) was epoxidized In the ^1H NMR spectrum of the diepoxy derivative (**2**) the H-8 signal was clearly observed at δ5 14 (J = 10, 5 5 and 4 5 Hz) The values of the coupling constants indicated the β-orientation for H-8, therefore the C-8 acetoxy group must be α From this reaction also the monoepoxy-derivative (**3**) was obtained Its ^1H NMR spectrum showed that only the signals for the C-15 protons were shifted to high field (δ3 31 and 2 88, AB)

The acetyl moiety was eliminated by saponification of **1a** producing **1b** in poor yield In the IR spectrum the carbonyl band for the ester function did not appear, instead, a hydroxyl absorption (3430 cm^{-1}) was observed The ^1H NMR spectrum showed the H-8 signal shifted to higher field (δ3 89) and partially superimposed with the H-6 signal The physical constants for this compound (**1b**) are almost identical with those of 8α-hydroxydehydrocostus lactone obtained from *Centaurea canariensis* [7, 8] [they only differ in the small additional coupling of the C-13 protons (δ6 25, *dd*, J = 3 5, 1 Hz and 6 14 *dd*, J = 3, 1 Hz)] The above mentioned facts permitted us to establish the structure of compound A as 8α-acetoxydehydrocostus lactone (**1a**)



R
1a Ac
1b H
1c Tig



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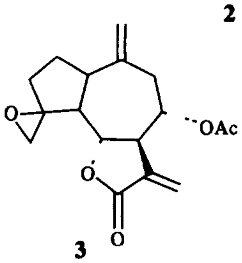

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Table 1 ^1H NMR spectral data of compounds **1–3** (80 MHz, $CDCl_3$, TMS as internal standard, values in parentheses are coupling constants in Hz)

	1a	**1b**	**1c**	**2**	**3**
H-6	3 98 *dd* (10, 9)	3 95 *dd* (10, 9)	4 03 *dd* (10, 9)	4 20 *dd* (11, 9)	4 1 *dd* (11, 9)
H-7	3 11 *m*	*	3 18 *m*	3 12 *m*	*
H-8	4 8–5 1*	3 90*	4 9–5 2*	5 14 *ddd* (10, 5 5, 4 5)	4 99*
H-13	6 18 *d* (3 5)	6 25 *dd* (3 5, 1)	6 18 *d* (3 5)	6 24 *d* (3 5)	6 2 *d* (3 5)
H-13′	5 61 *d* (3)	6 14 *dd* (3, 1)	5 59 *d* (3)	5 61 *d* (3)	5 58 *d* (3)
H-14	5 01 *sbr*	5 04 *br*	5 04 *br*	2 79 AB (2H)	5 13 *br*
H-14′	4 89 *sbr*	4 95 *br*	4 92 *br*		4 93 *br*
H-15	5 24 *sbr*	5 27 *br*	5 28 *br*	3 31 *d* (5)	3 31 *d* (5)
H-15′	5 06 *sbr*	5 06 *br*	5 1 *br*	2 90 *d* (5)	2 88 *d* (5)
OCOR′	2 11 *s* (3H)		6 92 *qbr* (7 5) 1 92 *dbr* (7 5) 1 79 *br*	2 12 (3H)	2 14 (3H)

*Superimposed signal

The minor component, compound B, $C_{20}H_{24}O_4$ (EM), mp 96–98°, $[\alpha]_D + 109\ 2°$ (*c*, 0 152, $CHCl_3$) obtained from the less polar fraction of the chromatography, also is an α,β-unsaturated-γ-lactone (1768 cm^{-1}) The ^1H NMR spectrum indicates a great similarity with that of compound A Compound B is esterified with a tigloyl residue instead of the acetyl of **1a** This was evident from the presence in the ^1H NMR spectrum of a broad quartet at δ 6 92 and two broad signals (3H each) at 1 92 and 1 79 The IR absorption band at 1713 cm^{-1} coupled with the mass peaks at m/z 228 $[M - 100]^+$, 83 (100) and 55 (11 5) confirmed this assumption and allowed us to assign the structure of 8α-tigloyloxydehydrocostus lactone (**1c**) for compound B, which is identical with ferreyanthus lactone [9]

EXPERIMENTAL

Aerial parts (3 3 kg) of *Gochnatia smithii* (voucher on deposit in the herbarium of the Instituto de Biología, U N A M, MEXU 342416) were extracted with $CHCl_3$ The crude gum (84 g) was percolated through a Tonsil column [10] 11 fractions were collected Fractions 1–8 ($CHCl_3$), 9–14 (EtOAc) Fractions 7–12 (18 4 g) were chromatographed over 550 g of silica gel (Merck 60, 70–230 mesh), 250 ml fractions were collected Fractions 27–49 ($CHCl_3$) gave, after crystallization from EtOAc–hexane, 79 6 mg of compound B (**1c**) mp 96–98°, $[\alpha]_D + 109\ 2°$ (*c* 0 152, $CHCl_3$), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1768, 1713, 1653 (calc for $C_{20}H_{24}O_4$, MW 328 Found MW (EIMS) 328) Other significant peaks in the MS were at m/z 228 $[M - C_5H_4O_2]^+$, 213 $[228 - Me]^+$, 83 (100), 55 (11 5)

Fractions 50–94 ($CHCl_3$) gave 3 6 g of compound A (**1a**) mp 120–121° (EtOAc–hexane), $[\alpha]_D\ + 87\ 3°$ (*c* 0 179, $CHCl_3$), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1768, 1735, 1652, 1640 (calc for $C_{17}H_{20}O_4$, MW 288 Found MW (EIMS) 288) Other relevant peaks in the MS were at m/z 246 $[M - C_2H_2O]^+$, 213 $[M - HOAc]^+$, 213 $[228 - Me]^+$, 91 (33 8), 43 (100)

Epoxidation of **1a** MCPBA (82 mg) was added to a soln of **1a** (68 4 mg) in $CHCl_3$ (8 ml) The mixture was oxidized at room temp for 40 hr The soln was diluted with $CHCl_3$, washed with satd $NaHCO_3$ soln and H_2O, dried and evaporated The residual gum exhibited two spots on TLC It was separated by prep TLC on silica gel (Me_2CO–hexane, 3 7, × 3) The substance with R_f 0 4 (28 mg) was **3** mp 148–151° (Me_2CO–hexane), IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1762, 1735, 1645, 1638 (calc $C_{17}H_{20}O_5$, MW 304 Found MW (EIMS) 304) Other significant peaks in the MS were at m/z 262 $[M - C_2H_2O]^+$, 244 $[M - HOAc]^+$, 229 $[244 - Me]^+$, 91 (100), 43 (69 7) The substance **2** with R_f 0 25 (21 mg) crystallized from Me_2CO–hexane, mp 238–240°, IR $\nu_{max}^{CHCl_3}$ cm^{-1} 1765, 1738, 1655 (calc for $C_{17}H_{20}O_6$, MW 320 Found MW (EIMS) 320) Other peaks in the MS were at m/z 290 $[M - CH_2O]^+$, 278 $[M - C_2H_2O]^+$, 260 $[M - HOAc]^+$ 240 $[M - CH_2O - C_2H_2O]^+$, 230 $[260 - CH_2O]^+$, 91 (73), 43 (100)

Hydrolysis of **1a** Compound **1a** (92 9 mg) was added to a soln of KOH (184 mg) in H_2O (10 ml) The mixture was left to stand at 60° for 1 hr with stirring The soln was neutralized with 10% H_2SO_4 soln, saturated with NaCl and extracted with EtOAc The washed and dried extract was evaporated and the solid residue was crystallized from Me_2CO–*i*-propyl ether–hexane to provide 30 4 mg of **1b**, mp 106–107°, $[\alpha]_D\ + 64\ 7°$ (*c* 0 295, $CHCl_3$), IR ν_{max}^{film} cm^{-1} 3430, 1765, 1658, 1645 (calc for $C_{15}H_{18}O_3$, MW 246 Found MW (EIMS) 246) Other MS peaks were at m/z 228 $[M - H_2O]^+$, 213 $[M - Me]^+$, 91 (100)

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HELIANGOLIDES AND BEJARANOLIDES FROM *CONOCLINIOPSIS PRASIIFOLIA*

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Key Word Index—*Conocliniopsis prasiifolia*, Compositae, sesquiterpene lactones, furoheliangolides, bejaranolides

Abstract—A reinvestigation of the aerial parts of *Conocliniopsis prasiifolia* afforded two furoheliangolides, conoprasiolide-9-*O*,5′-*O*-diacetate and 5′-desoxyconoprasiolide, as well as two bejaranolides, 9*β*-hydroxy-4*E*-bejaranolide and 3*α*,9*β*-dihydroxy-4*E*-bejaranolide The structures were elucidated by ^{1}H NMR spectroscopy The chemistry of *Conocliniopsis* supports the proposed close relationship to *Bejaranoa*

INTRODUCTION

The investigation of the new monotypic Brazilian genus *Conocliniopsis* (tribe Eupatorieae, subtribe Gyptidinae) [1] afforded furoheliangolides similar to those present in the closely related genus *Bejaranoa* [2, 3] The reinvestigation of the polar fractions of the aerial parts of *Conocliniopsis prasiifolia* (DC) K et R gave two further furoheliangolides and two bejaranolides which strongly supported the close relationship of this genus to *Bejaranoa* [4] The results will be discussed in this paper

RESULTS AND DISCUSSION

The aerial parts of *Conocliniopsis prasiifolia* afforded in addition to conoprasiolide (**1**) [2] and its 5′-*O*-acetate **2** [2] two further derivatives, the tiglate **3** and conoprasiolide-9-*O*,5′-*O*-diacetate (**4**) The structure of **3** followed from the molecular formula and the ^{1}H NMR spectral data (Table 1) which were close to those of **1** [2] and **2** [2] The difference in the nature of the ester groups in **1** and **3** at C-8 caused some small variations of chemical shifts, especially of H-6 and H-8, while the nature of the ester residue at C-8 clearly followed from the typical signals of a tiglate The diacetate **4** already was prepared by acetylation of **1** and **2** [2] Accordingly, the observed ^{1}H NMR spectral data (Table 1) were identical with those reported previously [2]

Furthermore, minute amounts of two additional sesquiterpene lactones were isolated The less polar lactone showed no molecular ion in the mass spectrum But as the ^{1}H NMR spectrum (Table 1) clearly displayed the characteristic signals of a tiglate, the observed peak at *m/z* 278 (corresponding to $C_{15}H_{18}O_5$) most likely was formed by elimination of tiglic acid Spin decoupling of the ^{1}H NMR spectrum allowed the assignment of all signals which showed a marked similarity to the spectrum of 4*E*-bejaranolide [3] However, the H-9 signals were replaced by a double doublet at δ4 36 Irradiation of this signal collapsed the doublet at 2 29 to a singlet and the signal at 5 86 to a doublet The latter was further coupled with the fourfold doublet at 2 85 Its irradiation caused the expected changes of the H-13 signals as well as that of H-6, and therefore was due to H-7 Addition of deuterium oxide collapsed the double doublet at 4 36 to a doublet while the doublet at 2 29 disappeared, thus indicating a hydrogen bonded hydroxy group at C-9, similar to the situation in **1** and **3** Accordingly, the stereochemistry at C-9 also was the same and all data agreed with the proposed structure **5**