Phytochemistry, Vol. 24, No. 12, pp. 3059–3060, 1985.
Printed in Great Britain.

0031–9422/85 \$3.00 + 0.00

ENT-PIMARADIENE DITERPENES FROM *GOCHNATIA GLUTINOSA*

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(*Received* 18 *March* 1985)

Key Word Index—*Gochnatia glutinosa*; Compositae; aerial parts; diterpenes; *ent*-pimaradiene; structural determination.

Abstract—Two diterpenes were isolated from the aerial parts of *Gochnatia glutinosa*. Their structures were established as *ent*-8(14),15-pimaradiene-3β,19-diol and as *ent*-8(14),15-pimaradiene-3β,18-diol by comparison of spectroscopic data with those of suitable model compounds.

INTRODUCTION

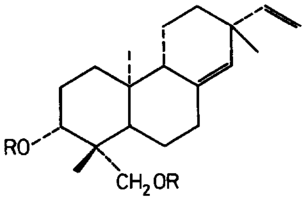
In an investigation of the natural products of plants endemic to the Argentinian region of Cuyo, we have examined *Gochnatia glutinosa* Don. The previous chemical work on five species of the large South American genus *Gochnatia* [1–4] revealed the presence of triterpenes (four species), sesquiterpene lactones (three species) and diterpenes (one species). The present investigation led to the isolation and identification of two *ent*-pimaradiene diterpenes.

RESULTS AND DISCUSSION

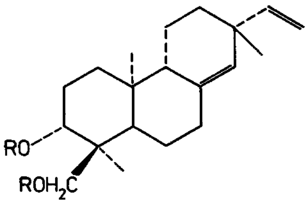
Systematic fractionation of a methanolic extract of the aerial parts of *G. glutinosa* led to the isolation of two crystalline diterpenes (**1a** and **2a**). The molecular formula of **2a** was determined as $C_{20}H_{32}O_2$ by mass spectrometry. Its IR spectrum showed primary and secondary hydroxyl groups (3400–3300, 1080, 1045 cm^{-1}), and mono and trisubstituted double bonds (995 and 915 cm^{-1} and 845 cm^{-1}, respectively). Its ^1H NMR spectrum showed the presence of three methyl groups (δ0.78, 0.90 and 0.98, 3H × 3 each), a proton geminal to an equatorial secondary hydroxyl group (δ3.58, *m*, 1H, $W_{1/2} = 18$ Hz), an AB system (δ3.36, 3.64, 2H, *dd*, $J = 11$ Hz) characteristic of an equatorial C-4 hydroxymethyl and four olefinic protons. Three of the olefinic peaks attributable to a monosubstituted olefin [5], constituted an ABX system (δ_A 4.90, δ_B 4.95, δ_X 5.73, $J_{AB} = 2$, $J_{AX} = 10$, $J_{BX} = 18$ Hz) while one was isolated (δ5.15) and weakly coupled. The olefinic proton region was very similar to those generally found in the 8(14),15-pimaradiene [6] skeleton. The mass spectrum contained ions at *m/z* 304 $[M]^+$, 286 $[M-H_2O]^+$, 273 $[M-CH_2OH]^+$, 271 $[M-Me-H_2O]^+$, 268 $[M-2H_2O]^+$, 255 $[M-H_2O-CH_2OH]^+$.

Treatment of **2a** with acetic anhydride–pyridine gave the diacetate **2b**, mp 68–69°, the ^1H NMR spectrum of which showed two acetoxy methyl signals at δ2.08, 2.00 while the methylene and methine signals were shifted to δ3.75 (*s*) and 4.76 (*m*). The above data were identical to those of 8(14),15-pimaradien-3β,18-diol [7], mp 180°, $[\alpha]_D = 106°$. However, the optical rotations, although of similar magnitude, were of opposite sign, −92.1° and −102° for **2a** and **2b**, respectively. On the basis of these observations, **2a** was identified as *ent*-8(14),15-pimaradiene-3β,18-diol.

The other diterpene, **1a**, $C_{20}H_{32}O_2$, gave rise to IR and mass spectra which closely resembled those of the **2a**, indicating that **1a** and **2a** were isomers. Comparison of the ^1H NMR spectra data of **1a** with those of **2a** showed differences of the chemical shifts for the methyl (δ0.66, 0.96 and 1.23, 3H × 3 each) and hydroxymethyl (δ3.43 and



Ia R = H
Ib R = Ac



2a R = H
2b R = Ac

Table 1. ^{13}C NMR spectral data for diterpenes **1a** and **2a** (25 MHz, $CDCl_3$, TMS as internal standard)

C	**2a**	**1a**
1	37.9 *t*	36.9 *t*
2	26.9 *t*	28.0 *t*
3	76.8 *d*	80.9 *d*
4	42.1 *s*	42.7 *s*
5	48.4 *d*	51.1 *d*
6	22.3 *t*	22.1 *t*
7	35.2 *t*	35.6 *t*
8	137.2 *s*	137.2 *s*
9	51.0 *d*	55.1 *d*
10	36.7 *s*	37.8 *s*
11	19.1 *t*	19.3 *t*
12	35.7 *t*	35.8 *t*
13	38.5 *s*	38.6 *s*
14	128.1 *d*	128.3 *d*
15	147.0 *d*	147.0 *d*
16	112.7 *t*	112.7 *t*
17	29.4 *q*	29.4 *q*
18	71.7 *t*	22.7 *q*
19	11.5 *q*	64.3 *t*
20	15.2 *q*	15.8 *q*

4.30, 2H, *dd*, $J = 11$ Hz) groups and the proton geminal to a hydroxyl group (δ3.45, 1H, *m*, $W_{1/2} = 18$ Hz).

The above data could be interpreted on the basis of a reversed configuration at C-4 [7]. The negative rotation of its diacetate **1b** $[\alpha]_D = -76°$, mp 68.5–69.5°, established the structure of **1a** as *ent*-8(14),15-pimaradiene-3β,19-diol. The ^{13}C NMR spectroscopic data of **1a** and **2a** were fully compatible with these assignments when the chemical shifts were compared with those of suitable model compounds [8–10].

EXPERIMENTAL

Mps: uncorr; ^1H NMR: 90 MHz, $CDCl_3$, TMS as internal standard; ^{13}C NMR: 25 MHz, $CDCl_3$, TMS as standard; MS: 70 eV, direct inlet; CC: silica gel; TLC: silica gel UV-254, solvent systems C_6H_6–dioxane–HOAc (45:5:1 and 90:25:4).

Plant material. Gochnatia glutinosa was collected in Canota (Mendoza, Argentina) and identified by José A. Ambrosetti (Voucher MERL 35083, IADIZA, Mendoza).

Extraction and isolation. The aerial parts (1400 g) were air-dried, finely ground and extracted at room temp. with MeOH (× 3, 24 hr). The crude extract obtained by evaporation at reduced pressure was dissolved in MeOH, which was treated with H_2O (10, 20 and 30%) then partitioned between *n*-hexane, CCl_4 and $CHCl_3$, respectively. The $CHCl_3$ extract (250 g) was adsorbed on silica gel (500 g) and after drying placed on the top of a column of silica gel packed in C_6H_6 and eluted with C_6H_6–EtOAc mixtures, to yield the following compounds in order of elution: **1a** (C_6H_6–EtOAc, 9:1) 0.650 g and **2a** (C_6H_6–EtOAc, 8:2) 0.470 g.

Ent-8(14),15-*pimaradiene*-3β,19-*diol* (**1a**). Colourless crystals from MeOH, mp 185.5–186.5°; $[\alpha]_D = -97.3°$ ($CHCl_3$; *c* 1.3); IR ν_{max}^{KBr} cm^{-1}: 3400–3300, 1080, 1045, 995, 915 and 850; ^1H NMR ($CDCl_3$): δ0.66, 0.96 and 1.23 (3H × 3 each, H-17, H-18 and H-20), 2.25 (1H, *m*, H-9), 3.43 and 4.30 (2H, AB, $J = 11$ Hz, H-19), 3.45 (1H, *m*, $W_{1/2} = 12$ Hz, H-3), 4.71–5.95 (4H, typical 8(14),15-pimaradiene double bond patterns [6]); MS *m/z* (rel. int.): 304, 2388 (calc. for $C_{20}H_{32}O_2$: 304. 2402) $[M]^+$ (11), 289 $[M-15]^+$ (2), 286 $[M-18]^+$ (22), 273 $[M-31]^+$ (6), 271 $[M-18-15]^+$ (7), 268 $[M-18-18]^+$ (5), 255 $[M-18-31]^+$ (23), 169 (8), 151 (21), 148 (31), 135 (33), 133 (56), 121 (100), 119 (45), 109 (48), 107 (61).

Ent-8(14),15-*pimaradiene*-3,19-*diacetate* (**1b**). Colourless crystals from C_6H_6–EtOAc (9:1), mp 68.5–69.5°; $[\alpha]_D = -76°$ ($CHCl_3$; *c* 1.2); IR ν_{max}^{KBr} cm^{-1}: 1745, 1630, 1245, 1040, 995, 920, 860; ^1H NMR ($CDCl_3$): δ0.73, 0.96 and 1.00 (3H × 3 each, H-17, H-18 and H-20), 2.03 (6H, *s*), 2.20 (1H, *m*, H-9), 4.13 and 4.39 (2H, AB, $J = 11$ Hz, H-19), 4.53 (1H, *m*, $W_{1/2} = 12$ Hz, H-3), 4.65–5.95 (4H, typical 8(14),15-pimaradiene double bond patterns [6]); MS *m/z* (rel. int.): 388 $[M]^+$ (18), 373 $[M-15]^+$ (4), 328 $[M-60]^+$ (14), 268 $[M-60-60]^+$ (20), 255 (10), 253 (12), 148 (13), 133 (100), 121 (22), 119 (64), 109 (12), 107 (24).

Ent-8(14),15-*pimaradiene*-3β,18-*diol* (**2a**). Colourless crystals (Me_2CO), mp 178–179°; $[\alpha]_D = -92°$ ($CHCl_3$; *c* 1.5); IR ν_{max}^{KBr} cm^{-1}: 3400–3300, 1080, 1045, 995, 915, 845; ^1H NMR ($CDCl_3$): δ0.78, 0.90 and 0.98 (3H × 3 each, H-17, H-19 and H-20), 2.23 (1H, *m*, H-9), 3.36 and 3.64 (2H, AB, $J = 11$ Hz, H-18), 3.58 (1H, *m*, $W_{1/2} = 18$ Hz, H-3), 4.65–6.00 (4H, typical 8(14),15-pimaradieno double bonds patterns [6]); MS *m/z* (rel. int.): 304.2371 (calc. for $C_{20}H_{32}O_2$: 304.2402) $[M]^+$ (16), 289 $[M-15]^+$ (10), 286 $[M-18]^+$ (26), 273 $[M-31]^+$ (27), 271 $[M-18-15]^+$ (22), 268 $[M-18-18]^+$ (2), 255 $[M-18-31]^+$ (13), 169 (10), 151 (27), 148 (29), 135 (39), 133 (49), 121 (100), 119 (47), 109 (57), 107 (58).

Ent-8-(14),15-*pimaradiene*-3β,18-*diacetate* (**2b**). Colourless crystals (MeOH), mp 68–69°; $[\alpha]_D = -102°$ ($CHCl_3$; *c* 0.95); IR ν_{max}^{KBr} cm^{-1}: 1740, 1635, 1250, 1040, 995, 920, 865; ^1H NMR: δ0.76, 0.83 and 0.95 (3H × 3 each, H-17, H-19 and H-20), 2.00 and 2.05 (3H × 2 each), 2.25 (1H, *m*, H-9), 3.75 (2H, *s*, H-18), *ca* 4.76 (1H, obscured, *m* (*br*), H-3), 4.70–5.95 (4H, typical 8(14),15-pimaradiene double bonds patterns); MS (rel. int.) *m/z*: 388 $[M]^+$ (25), 373 $[M-15]^+$ (10), 328 $[M-60]^+$ (18), 268 $[M-60-60]^+$ (23), 255 (17), 253 (15), 148 (17), 133 (100), 121 (27), 119 (64), 109 (15), 107 (26).

Acknowledgements—We thank Prof. Juan Kavka and Lic. Federico H. Guidugli, LEA, University of San Luis, for the mass spectra, and Ing. José A. Ambrosetti, IADIZA, Mendoza, for plant collection and botanic assistance. This work was supported by a grant from CONICET.

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