REFERENCES

1. Shutt, D. A. (1976) *Endeavour* **35**, 110.
2. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1974) *Supplement of Glossary of Indian Medicinal Plants*, p. 97. CSIR, New Delhi.
3. Narayana, V. and Seshadri, T. R. (1971) *Indian J. Chem.* **9**, 14.
4. Wagner, H. and Seligman, O. (1973) *Tetrahedron* **29**, 3029.
5. Ansari, F. R., Ansari, W. H., Rahman, W., Seligman, O., Chari, V. M., Wagner, H. and Osterdahl, B. (1979) *Planta Med.* **36**, 196.
6. Brimacombe, J. S., Jones, B. P., Stacey, M. and Willard, J. J. (1966) *Carbohydr. Res.* **2**, 167.

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TWO 12a-HYDROXYROTENOIDS FROM *BOERHAAVIA COCCINEA*

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Key Word Index—*Boerhaavia coccinea*; Nyctaginaceae; roots; 12a-hydroxyrotenoids; ^{13}C NMR.

Abstract—Two new 12a-hydroxyrotenoids, (−)-4,11,12a-trihydroxy-9-methoxyrotenoid and (−)-4,9,11,12a-tetrahydroxyrotenoid, were isolated from the roots of *Boerhaavia coccinea*. Their structures were established by spectroscopic methods.

INTRODUCTION

Boerhaavia coccinea is a Brazilian plant known by the trivial name of pega-pinto. The roots are used in traditional medicine for the treatment of liver, loins and urinary diseases [1]. Only two species of *Boerhaavia* have been extensively studied, *B. repens* [2, 3] and *B. diffusa* [4], from which alkaloids and polysaccharides have been isolated. In this paper we report the isolation of (−)-4,11,12a-trihydroxy-9-methoxyrotenoid (**1**) and (−)-4,9,11,12a-tetrahydroxyrotenoid (**2**) from a methanolic extract of roots of *B. coccinea*.

RESULTS AND DISCUSSION

Compound **1**, $C_{17}H_{14}O_7$, $[M]^+$ at *m/z* 330, $[\alpha]_D^{20}$ −339°, was obtained as an amorphous powder. It showed UV maxima (MeOH) at 340 (sh), 293 and 216 nm, and IR bands ($CHCl_3$) at 3550 (br, OH) and 1630 cm^{-1} (chelated C=O). The ^{1}H NMR spectrum of **1** exhibited the signals of five aromatic protons, two of which were *meta*-coupled (δ6.08 and 6.10, 2H, 2*d*, J = 2 Hz), a methoxyl group (δ3.86, 3H, *s*), a chelated hydroxyl (δ11.85, 1H, *s*, exchangeable with D_2O) and an ABC system (δ4.44, 1H, *dd*, J = 5.5 and 10 Hz; δ4.48, 1H, *t*, J = 10 Hz; δ4.77, 1H, *dd*, J = 5.5 and 10 Hz), attributed to a O–CH_2–CH–O sequence. In agreement with the latter assignment, the ^{13}C NMR spectrum of **1** (see Experimental) showed resonances at 77.1 and 62.4 ppm (doublet and triplet, respectively, in the off-resonance decoupled ^{13}C NMR spectrum), together with a signal at 67.0 ppm (singlet).

The aforementioned data suggested for **1** the structure of a 12a-hydroxyrotenoid. After acetylation, **1** was transformed into the corresponding derivative **3**, $C_{23}H_{20}O_{10}$, which showed in its ^{1}H NMR spectrum the signals of an aliphatic acetyl group (δ1.88), assigned to the 12a position, and two aromatic acetyl groups (2.29 and 2.37).

In the mass spectrum of **1** the base peak at *m/z* 167 ($C_8H_7O_4$) originated from the typical retro-Diels–Alder fragmentation of 6a,12a-saturated rotenoids [5], thus confirming the suggested structure and the assignment of the methoxyl and the chelated hydroxyl group to the D-ring (Scheme 1). On account of the presence in the ^{1}H NMR spectrum of **1** of a low-field shifted signal (δ7.78, 1H, *dd*, J = 3 and 7 Hz), the third hydroxyl group could be located on C-4 and, therefore, the structure of 4,11,12a-trihydroxy-9-methoxyrotenoid was unambiguously assigned to **1**. The *trans*-B/C ring junction was assigned to **1** on the basis of the H-1 chemical shift value [6], whereas it was impossible to correlate the Cotton effect curve to the absolute configuration on account of the absence of proper models. Compound **2**, $C_{16}H_{12}O_7$, $[M]^+$ at *m/z* 316, crystals from $CHCl_3$–MeOH, mp 237–240°, $[\alpha]_D^{20}$ −440°, exhibited UV maxima (MeOH) at 335 (sh), 293 and 231 nm. The structure of a 9-demethyl derivative of **1** could be assigned to **2** by comparison of the ^{1}H NMR and mass spectra of the two compounds (see Experimental). Moreover, **1** and **2** when treated with diazomethane gave the same methyl derivative by TLC comparison.

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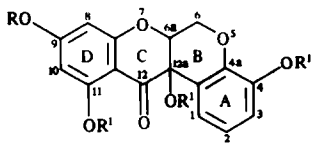
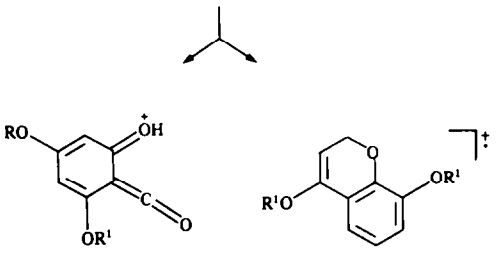


	R	R¹
1	Me	H
2	H	H
3	Me	Ac



R	R¹		
Me	H	$C_8H_7O_4$ *m/z* 167	R¹ = H $C_9H_8O_3$ *m/z* 164
H	H	$C_7H_5O_4$ *m/z* 153	

Scheme 1. Mass spectral fragmentation of rotenoids **1** and **2**.

It is interesting to note the unusual monosubstitution of compounds **1** and **2** on the A-ring, i.e. 2,3-disubstituted in all of the 12a-hydroxyrotenoids isolated up to now. To our knowledge, this is the first report of the isolation of 12a-hydroxyrotenoids from the Nyctaginaceae.

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively (TMS as internal standard). TLC was carried out on silica gel F_{254}. Elemental analyses were in agreement with the molecular formulae.

Plant material. Roots of *B. coccinea* Mill. were collected in Maceiò, Alagoas (Brazil) in October 1984 and identified by one of us (E.G. SA); a voucher sample (BC 85) has been deposited at the Herbarium of Centro Chimica dei Recettori del C.N.R.

Isolation. Dried roots (1.7 kg) were extracted at room temp. with MeOH. The residue after evaporation (15 g) was chromatographed on silica gel using a $CHCl_3$–MeOH gradient. The fractions eluted with 4% and 8% MeOH were re-chromatographed on silica gel (hexane–EtOAc, 3:1) giving pure **1** (60 mg) and **2** (25 mg).

Compound **1**. Amorphous powder, $[\alpha]_D^{20}$ −339° (*c* 1.1; MeOH); UV λ_{max}^{MeOH} nm: 340 (sh), 293 and 216; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 1630, 1530. ^1H NMR (CD_3COCD_3): δ3.86 (3H, *s*, OMe), 4.44 (1H, *dd*, J_{6eq-6a} = 5.5 and $J_{6eq-6ax}$ = 10 Hz, H-6eq), 4.48 (1H, *t*, J_{6ax-6a} = 10 Hz, H-6 ax), 4.77 (1H, *dd*, H-6a), 6.08 (1H, *d*, *J* = 2 Hz, H-8 or H-10), 6.10 (1H, *d*, H-10 or H-8), 6.84–6.87 (2H, *m*, H-2 and H-3), 7.78 (1H, *dd*, *J* = 3 and 7 Hz, H-1), 11.85 (1H, *s*, exch. D_2O, OH). ^{13}C NMR (CD_3COCD_3): 194.9 (C-12), 168.9 (C-9), 166.3 (C-7a), 162.8 (C-11), 146.5 (C-4a)*, 143.8 (C-4)*, 122.8 (C-2)†, 121.6 (C-3)†, 121.5 (C-12b), 116.8 (C-1), 103.0 (C-11a), 96.2 (C-8), 94.4 (C-10), 77.1 (C-6a), 67.0 (C-12a), 62.4 (C-6), 56.4 (OMe). EIMS *m/z* (rel. int.): 330 $[M]^+$ ($C_{17}H_{14}O_7$) (23), 312 $[M-H_2O]^+$ (3), 181 (29), 168 (14), 167 $[C_8H_7O_4]^+$ (100), 164 (13), 163 (30), 137 (9). CD (MeOH), $\theta(\lambda_{max}$, nm): −9770 (341), +5940 (318), −16630 (288).

Compound **1** was acetylated with a mixture of pyridine and Ac_2O at 100° for 1 hr. After evaporation of reagents and CC of the residue (silica gel, hexane–EtOAc, 4:1), pure **3** was obtained. Oil. ^1H NMR ($CDCl_3$): δ1.88, 2.29 and 2.37 (9H, 3*s*, 3OCOMe), 3.81 (3H, *s*, OMe), 4.46–4.55 (2H, *m*, H-6ax and H-6eq), 4.71 (1H, *m*, H-6a), 6.35 (1H, *d*, *J* = 2 Hz, H-8 or H-10), 6.36 (1H, *d*, H-10 or H-8), 7.00 (1H, *t*, *J* = 7 Hz, H-2), 7.06 (1H, *dd*, *J* = 2 and 7 Hz, H-3), 7.98 (1H, *dd*, H-1). EIMS *m/z* (rel. int.): 456 $[M]^+$ ($C_{23}H_{20}O_{10}$) (6), 414 (11), 372 (13), 355 (8), 312 (35), 285 (12), 284 (21), 209 (68), 206 (9), 205 (17), 167 (100), 164 (25).

Compound **2**. Crystals from $CHCl_3$–MeOH, mp 237–240°, $[\alpha]_D^{20}$ −440° (*c* 0.9; MeOH); UV λ_{max}^{MeOH} nm: 335 (sh), 293 and 231. ^1H NMR (CD_3COCD_3): δ4.44–4.50 (2H, *m*, H-6ax and H-6eq), 4.77 (1H, *dd*, *J* = 6 and 10 Hz, H-6a), 6.01 (1H, *d*, *J* = 2 Hz, H-8 or H-10), 6.02 (1H, *d*, H-10 or H-8), 6.84–6.86 (2H, *m*, H-2 and H-3), 7.80 (1H, *dd*, *J* = 3 and 6.5 Hz, H-1), 11.90 (1H, *s*, exch. D_2O, OH). EIMS *m/z* (rel. int.): 316 $[M]^+$ ($C_{16}H_{12}O_7$) (28), 298 $[M-H_2O]^+$ (1), 164 (19), 163 (40), 153 $[C_7H_5O_4]^+$ (100), 137 (11). CD (MeOH), $\theta(\lambda_{max}$, nm): −2010 (338), +1150 (310), −2750 (288).

*,†These signals may be interchanged.

REFERENCES

1. Braga, R. (1960) *Plantas do Nordeste, Especialmente do Ceará*, p. 406. Imprensa official, Fortaleza, Ceará, Brazil.
2. Nandi, R. P. and Chatterjee, S. K. (1974) *Indian J. Exp. Biol.* **12**, 509.
3. Haq, Q. N. and Haq, N. (1975) *Bangladesh J. Sci. Ind. Res.* **10**, 84; (1975) *Chem. Abstr.* **83**, 190364 f.
4. Gupta, D. R. and Ahmed, B. (1984) *Indian J. Chem.* **23B**, 682.
5. Reed, R. I. and Wilson, J. M. (1963) *J. Chem. Soc.* 5949.
6. Crombie, L. and Lown, J. W. (1962) *J. Chem. Soc.* 775.