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TWO NEW ISOFLAVONOIDS FROM *BOERHAAVIA COCCINEA*¹

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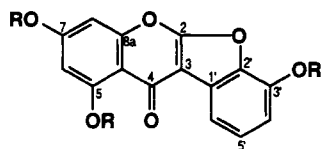
ABSTRACT.—From the roots of *Boerhaavia coccinea*, 5,7,3'-trihydroxycoumaronochromone [**1**] and 6,9,11-trihydroxy-6a,12a-dehydrorotenoid [**2**] were isolated. Their structures were established on the basis of spectral evidence.

Previously, we reported the isolation and structure determination of two new 12a-hydroxyrottenoids from the roots of *Boerhaavia coccinea* Mill. (Nyctaginaceae) (1). Further examination of the same extract led to the isolation of two new minor components identified as 5,7,3'-trihydroxycoumaronochromone (coccineone A) [**1**], and 6,9,11-trihydroxy-6a,12a-dehydrorotenoid (coccineone B) [**2**].

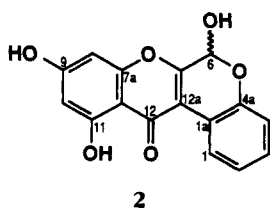
The molecular formula $C_{15}H_8O_6$ was assigned to **1** on the basis of eims, $[M]^+$ at m/z 284, and ^{13}C -nmr data. The position and relative intensities of the peaks of the uv spectrum [λ max at 320, 254, and 222 (sh) nm] suggested an isoflavone structure for **1**. Moreover, the absence in the 1H -nmr spectrum of a signal ca. 8

ppm due to H-2 was indicative of a coumaronochromone skeleton. Compound **1** by treatment with pyridine and Ac_2O gave a triacetate **3**, $[M]^+$ at m/z 410. Two of the three OH groups of **1** were located at C-5 and C-7 on the basis of the following evidence: first, the presence in the 1H -nmr spectrum of **1** of a signal at δ 12.48, attributed to the C-5 chelated hydroxy group, and second, the bathochromic shift of 8 nm (Band II) observed in the uv spectrum of **1** on addition of NaOAc, due to the C-7 hydroxy group (2). The two doublets *meta*-coupled that resonated at δ 6.29 and 6.55 in the 1H -nmr spectrum of **1** were thus assigned to H-6 and H-8, respectively. The remaining signals of the 1H -nmr spectrum of **1** belonging to a 1,2,3-trisubstituted benzene ring excluded the 4' and 5' positions for the third hydroxy group. Between the two remaining possibilities, the H-6' was discarded on the basis of an observed doublet at δ 7.36, therefore assigning it to H-3' (3). The structure of **1** was thus determined as 5,7,3'-trihydroxycoumaronochromone. To our knowledge this is the first example of the isolation of a coumaronochromone from members of the Nyctaginaceae.

To compound **2** the molecular formula $C_{16}H_{10}O_6$ was assigned on the basis of eims ($[M]^+$ at m/z 298) and ^{13}C -nmr data. Uv maxima of **2** were in agreement with a dehydrorotenoid structure. In the 1H -nmr spectrum of **2** the signals due to a hydrogen-bonded OH group (s,



- 1** R=H
3 R=Ac



¹Dedicated to Prof. G.B. Marini-Bettolo on the occasion of his 75th birthday.

δ 12.87), and an alcoholic OH group (bs, δ 4.20), both exchangeable with D_2O , were present. The latter was attributed to an hemiacetalic function located at C-6. This assignment for **2** was in agreement with the signals at 89.5 ppm and δ 6.08 (1H, s) in the ^{13}C - and 1H -nmr spectra, respectively, as well as the fragment ions at m/z 281 $[M - OH]^+$ and 268 $[M - CHO]^+$.

The presence in the 1H -nmr spectrum of **2** of two *meta*-coupled protons (δ 6.21 and 6.33, 2H, 2d, $J = 2.0$ Hz), and four aromatic protons belonging to an ABCD system (see Experimental) accounted for a 9,11-disubstituted D ring and an unsubstituted A ring, assigning the structure **2** to coccineone B. Only a few examples of 6-substituted dehydrorotenoids have been so far described in the literature. It is interesting to note that only the four representatives isolated from the Nyctaginaceae [boeravinones A and B (4), repenone (5), and coccineone B] show an unsubstituted A ring, whereas a 2,3-substitution pattern is common to the rotenoid analogues isolated from the Leguminosae and Stemonaceae.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.— 1H - and ^{13}C -nmr spectra were obtained at 400 and 100 MHz, respectively, on a Bruker AM 400 (TMS as internal standard).

EXTRACTION AND SEPARATION.—The roots of *B. coccinea*, collected and identified as previously described, were extracted as reported in Messana *et al.* (1). A voucher specimen (BC 85) has been deposited at the herbarium of Centro Chimica dei Accettori (CNR). The MeOH extract (15 g) was chromatographed on Si gel 60 using a $CHCl_3$ /MeOH gradient. The fraction eluted with 8% MeOH, rechromatographed using $CHCl_3$ -*n*-hexane (8:2), gave pure **1** (60 mg) and **2** (62 mg).

COCCINEONE A [1].—Crystals from CH_2Cl_2 /MeOH: mp $> 310^\circ$; uv λ max (MeOH) nm (log ϵ) 320 (3.98), 254 (4.42), 222 sh (4.50); λ max (MeOH + NaOAc) 341, 262, 222 sh; 1H nmr (DMSO- d_6) δ 6.29 (1H, d, $J = 2.0$ Hz, H-6), 6.55 (1H, d, $J = 2.0$ Hz, H-8), 6.92 (1H, bd,

$J = 8.0$ Hz, H-4'), 7.24 (1H, dd, $J = 8.0, 7.8$ Hz, H-5'), 7.36 (1H, bd, $J = 7.8$ Hz, H-6'), 12.84 (1H, s, exch. with D_2O , OH); ^{13}C nmr (DMSO- d_6) δ 178.7 (C-4), 164.5^a (C-2), 164.3^a (C-7), 162.0^a (C-5), 154.8 (C-8a), 142.5 (C-3'), 137.1 (C-2'), 126.1 (C-5'), 123.6 (C-3), 112.7^b (C-6'), 110.8^b (C-4'), 102.4 (C-4a), 99.8 (C-6), 97.1 (C-1'), 95.1 (C-8) (signals with the same superscript may be interchanged); eims m/z $[M]^+$ 284 (100%), 255 (7), 149 (46).

COCCINEONE A TRIACETATE [3].—Compound **1** was treated with Ac_2O and pyridine to give an amorphous triacetate **3**: 1H nmr ($CDCl_3$) δ 2.36, 2.43, and 2.50 (9H, 3s, 3 OAc), 6.98 (1H, d, $J = 2.0$ Hz, H-6), 7.17 (1H, bd, $J = 8.0$ Hz, H-4'), 7.40 (1H, d, $J = 2.0$ Hz, H-8), 7.41 (1H, dd, $J = 8.0, 7.8$ Hz, H-5'), 8.01 (1H, bd, $J = 7.8$ Hz, H-6'); eims m/z $[M]^+$ 410 (3%), 326 (36), 284 (100), 255 (22).

COCCINEONE B [2].—Crystals from CH_2Cl_2 /MeOH: mp $> 310^\circ$; uv λ max (MeOH) nm (log ϵ) 330 (3.58), 300 (3.93), 268 (4.33), 214 (4.36); $[\alpha]^{25}_D$ 0 ($c = 1.0$, Me_2CO); 1H nmr (CD_3COCD_3) δ 4.20 (1H, bs, exch. with D_2O , OH), 6.08 (1H, s, H-6), 6.21 (1H, d, $J = 2.0$ Hz, H-8), 6.33 (1H, d, $J = 2.0$ Hz, H-10), 6.97 (1H, dd, $J = 8.0, 1.3$ Hz, H-4), 7.01 (1H, ddd, $J = 7.8, 7.3$, and 1.3 Hz, H-2), 7.20 (1H, ddd, $J = 8.0, 7.3$, and 1.7 Hz, H-3), 8.71 (1H, dd, $J = 7.8, 1.7$ Hz, H-1), 12.87 (1H, s, exch. with D_2O , OH); ^{13}C nmr (CD_3COCD_3) δ 181.2 (C-12), 165.5 (C-9), 163.7 (C-11), 158.0 (C-7a and C-6a), 149.9 (C-4a), 129.5 (C-3), 127.6 (C-1), 122.9 (C-2), 118.1 (C-4), 117.7 (C-1a), 110.1 (C-12a), 106.1 (C-11a), 100.4 (C-10), 94.9 (C-8), 89.5 (C-6); eims m/z $[M]^+$ 298 (50%), 281 (15), 269 (100).

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