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A methylenedioxyflavonol from aerial parts of *Blutaparon portulacoides*

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Abstract

The aerial parts from *Blutaparon portulacoides* yielded a flavonol whose structure was established as 3,5,3′-trihydroxy-4′-methoxy-6,7-methylenedioxyflavone. In addition, the aerial parts yielded the isoflavone irisone B and the steroids stigmasterol, sitosterol and campesterol. The roots of *B. portucaloides* furnished sitosteryl, stigmast-7-enyl and spinasteryl β-D-glucopyranosides as well as vanillic acid. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *Blutaparon portulacoides*; Amaranthaceae; Capotiragua; Methylenedioxyflavonol

1. Introduction

The Amaranthaceae comprises approximately 65 genera and 1000 species of annual and perennial herbaceous plants, shrubs and some trees occurring in tropical, subtropical and temperate regions (Siqueira, 1994/1995). Chemical characterization shows the occurrence of chromoalkaloids, ecdysteroids, betaines, betacyanines, saponins, flavonoids, triterpenes (Pomilio, Solá, Mayer & Rumi, 1994; Banerji, Chintalwar, Joshi & Chadha, 1971; Busch & Pomilio, 1982; Heuer, Wray, Metzger & Strack, 1992; Young, Potomati, Chu, Haraguchi, Yamamoto & Kawano, 1997; Shiobara et al., 1993) and steroids, with a predominance of Δ^7-sterols (Patterson, Xu & Salt, 1991). Some plants of the family are used because of their nutritive and medicinal value (Gorinstein, Moshe, Greene & Arruda, 1991; Si-Man, Yong-Sheng, Tabba & Smith, 1988). *B. portulacoides* (Gomphreneae) is a well-known species, commonly found on the beach sands of the eastern coast of Brazil (Farias & Flores, 1989), where it is popularly known as capotiraguá (Siqueira, 1987). This work reports the determination of the structure of a novel flavonol from *B. portucaloides* by spectroscopic method. Other compounds identified were irisone B (Chiji, Arakawa, Veda, Kuroda & Izwa, 1986), sitosteryl, stigmast-7-enyl and spinasteryl β-D-glucopyranosides (Kojima, Sato, Hatano & Ogura, 1990), vanillic acid (Sakushima, Coskum & Maoka, 1995) and the steroids stigmasterol, sitosterol and campesterol.

2. Results and discussion

The UV (260, 356 nm), IR (1683 cm^{-1}. C=O) and absence of a singlet relative to C-3 proton in the ^{1}H-NMR spectra, indicated that **1** is a flavonol. The ^{1}H-NMR signals and a singlet integrate to three protons at δ 3.84, showing the presence of three free hydroxyl groups (which disappeared upon addition of D_2O), and a methoxyl group, respectively. In the aromatic proton region, two doublets at δ 7.69 (J = 2.1 Hz) and 7.08 (J = 8.5 Hz) and a double doublet at δ 7.65 (J = 8.5; 2.1 Hz) were observed. suggesting a B ring sub-

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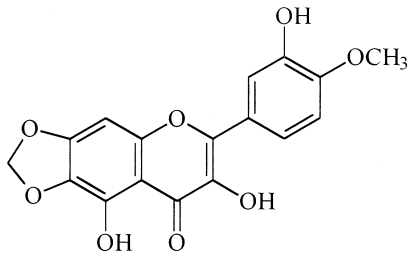
stituted at positions 3′ and 4′. The MS-fragmentation ion at m/z =151 disclosed that one hydroxyl group and the methoxyl group were in ring B.

The irradiation of the methoxyl group in the NOE experiment and a bathochromic shift of band I with decreased intensity observed in the UV spectra upon addition of NaOH, showed that it was at position C-4′ (Mabry, Markham & Thomas, 1970).

The ^{1}H-NMR signal at δ 6.1 (2H, *s*), ^{13}C-NMR signal at δ 102.9 and IR absorption band at 932 cm^{-1}, revealed the presence of a methylenedioxy group in **1**.



1

The position of this group on ring A was suggested to be between C-6 and C-7 owing to a signal at 89.6 observed in ^{13}C-NMR: it was assigned to the C-8 carbon following comparison with 5,3′,4′-trihydroxy-3-methoxy-6,7-methylenedioxyflavone 4′-β-D-glucuronide (Aritomi & Kawasaki, 1984). Thus **1** must be 3,5,3′-trihydroxy-4′-methoxy-6,7-methylenedioxyflavone.

To conclude, 3,5,3′-trihydroxy-4′-methoxy-6,7-methylenedioxyflavone, isolated from the aerial parts of *B. portulacoides*, is a derivative of gomphrenol (first isolated by Bouillant, Redolfi, Cantisani & Chopin, 1978), from leaves of *Gomphrena globosa* — Amaranthaceae). Irisone B. also isolated from aerial parts of *B. portulacoides*, is an isoflavone that also contains a methyenedioxy group on ring A (Chiji et al., 1986). Flavonoids and isoflavonoids bearing the methylenedioxy group on ring A are rare in nature (Bouillant et al., 1978; Boland & Donnelly, 1998).

3. Experimental

3.1. General

Mps: uncorr. UV: MeOH; IR: KBr disc.NMR in DMSO-d_6 with TMS as int. standard; MS: Hewlett–Packard Model 5988A, direct inlet at 70 eV.

3.2. Plant material

Blutaparon portulacoides (St. Hil) Mears was collected at Restinga de Maricá, Rio de Janeiro, RJ, Brazil, in January 1995, and identified by Prof. J.C. de Siqueira (Pontifica Universidade Catolica, Rio de Janeiro): a voucher specimen was deposited at the Herbarium of the Departament of Biology of the School of Sciences of FFCLRP-USP (SPSR 02961).

3.3. Extraction and isolation procedures

The aerial parts of plants were dried, powdered and exhaustively extracted using successively, hexane, EtOAc and EtOH. The solvent of each extraction was vacuum evaporated. To obtain **1**, 500.0 g of the dried, crude EtOH extract were partitioned and 4.3 g of the material from the EtOAc extract, were again partitioned using successively, hexane and CH_2Cl_2. The CH_2Cl_2 extract (3.1 g) was fractionated by CLV (Kieselgel 60H, 310 g) and eluted with a gradient of hexane, EtOAc and MeOH, yielding 22 mg of substance. It was crystallized in DMSO.

3.4. 3,5,3′-Trihydroxy-4′-methoxy-6,7-methylenedioxyflavone

Yellow needles, mp 264–267° EIMS 70 eV m/z (rel. int.): 344 $[M]^+$ (100), 329 $[M–Me]^+$ (49), 151 $[M-193]^+$ (17): $UV_{\lambda_{max}^{MeOH}}$ (nm): 260, 356; $^+AlCl_3$: 268, 386; $^+AlCl_3$ ^+HCl: 221, 270, 384, 421; ^+NaOAc: 258, 346; ^+NaOAc $^+H_3BO_3$: 262, 358; ^+NaOH: 231, 274, 408; ^{1}H-NMR (300 MHz, DMSO-d_6): δ 3.84 (3H, *s*, –OMe), 6.15 (2H, *s*, $–OCH_2O–$), 6.88 (1H, *s*, H-8), 7.08 (1H, *d*, J =8.5 Hz, H-5′), 7.65 (1H, *dd*, J =8.5 and 2.1 Hz, H-6′), 7.69 (1H, *d*, J =2.1 Hz, H-2′), 9.34 (*s*, OH-3 or 3′), 9.57 (*s*, OH-3′ or 3) and 12.45 (*s*, OH-5); ^{13}C-NMR (75 MHz, DMSO-d_6): 55.8 (–OMe), 89.6 (C-8), 102.9 ($–OCH_2O–$), 106.1 (C-10), 111.9 (C-5′), 114.9 (C-2′), 120.0 (C-6′), 123.5 (C-1′), 129.0 (C-6), 136.5 (C-3), 140.0 (C-2), 146.4 (C-3′), 147.2 (C-5), 149.7 (C-4′), 151.8 (C-7), 154.1 (C-9), 176.6 (C-4).

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