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Anadanthoside: a flavanol-3-*O*-β-D-xylopyranoside from *Anadenanthera macrocarpa*

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Abstract

The new fisetinidol-3-*O*-β-D-xylopyranoside, named anadanthoside, was isolated from the bark of *Anadenathera macrocarpa* (Leguminosae). The structure was assigned by FABMS and 2D NMR analysis. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Anadenanthera macrocarpa; Leguminosae; Fisetinidol-3-*O*-β-D-xylopyranoside

1. Introduction

As a part of our continuing studies (Piacente et al., 1994; Piacente, Pizza, De Tommasi, & De Simone, 1996; Piacente, Belisario, Del Castillo, Pizza, & De Feo, 1998; De Tommasi et al., 1998) on new potentially bioactive compounds from South American medicinal plants, we investigated the bark of *Anadenanthera macrocarpa*. (Leguminosae), a medicinal plant which is used to treat dysentery, as vermifuge and antipyretic. Furthermore, the bark of *A. macrocarpa* is used by the Mosetene ethnic group North of La Paz, Bolivia, to tan leather (Vargas & Quintana).

Separation of the components of the $CHCl_3$/MeOH (9:1) extract of the bark of *A. macrocarpa* by Sephadex LH-20 yielded as the main compound the new fisetinidol-3-*O*-β-D-xylopyranoside (**1**). The molecular formula ($C_{20}H_{22}O_9$) of **1** was determined by ^{13}C, DEPT ^{13}C NMR analysis (Table 1) and FABMS in negative ion mode, which gave a quasi molecular anion $[M-H]^-$ at m/z 405 and prominent fragments at m/z 273 $[(M-H)-132]^-$ due to the cleavage of a pentose unit with or without the glycosidic oxygen. The ^1H NMR spectrum displayed in the aromatic region proton signals at δ 6.72 (1H, *dd*, $J=2.0$ and 8.3 Hz, H-6′), 6.76 (1H, *d*, $J=8.3$ Hz, H-5′) and 6.82 (1H, *d*, $J=2.0$ Hz, H-2′) ascribable to a 1′,3′,4′-trisubstituted ring B of a flavonoid skeleton (Bae, Burger, Steynberg, Ferreira, & Hemingway, 1993) and signals at δ 6.33 (1H, *d*, $J=2.0$ Hz, H-8), 6.36 (1H, *dd*, $J=2.0$ and 8.3 Hz, H-6) and 6.85 (1H, *d*, $J=8.3$ Hz, H-5) suggesting the occurrence of only one hydroxyl group at C-7 of ring A (Nunes, Haag, & Bestmann, 1989). Further features were signals at δ 2.82 (1H, *dd*, $J=6.2$ and 15.6 Hz) and 2.87 (1H, *dd*, $J=4.8$ and 15.6 Hz), typical of H_2-4 of a flavane derivative, and at δ 3.10 (1H, *dd*, $J=7.3$ and 8.7 Hz), 3.15 (1H, *t*, $J=11.4$ Hz),

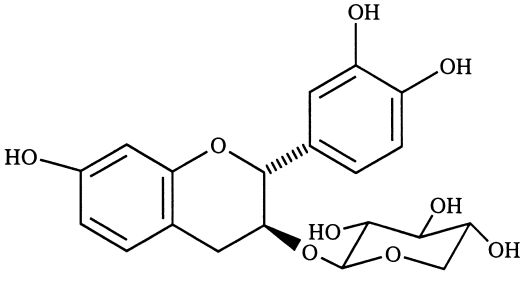

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Table 1
^1H and ^{13}C NMR data of **1** in CD_3OD (δ)[a]

	δ_H (*J* in Hz)	δ_C
Aglycone		
2	4.97, *d* (5.9)	80.7
3	4.15, *m*	76.9
4	2.82, *dd* (6.2, 15.6)	31.0
	2.87, *dd* (4.8, 15.6)	
5	6.85, *d* (8.3)	131.5
6	6.36, *dd* (2.0, 8.3)	109.6
7	–	158.0
8	6.33, *d* (2.0)	103.5
9		155.9
10		112.4
1′	–	132.2
2′	6.82, *d* (2.0)	114.8
3′	–	146.3
4′	–	146.4
5′	6.76, *d* (8.3)	116.3
6′	6.72, *dd* (2.0, 8.3)	119.6
xylose		
1	4.16, *d* (7.3)	105.2
2	3.10, *dd* (7.3, 8.7)	75.0
3	3.23, *t* (8.7)	77.6
4	3.45, *ddd* (6.2, 8.7, 11.4)	71.4
5	3.15, *t* (11.4)	66.8
	3.85, *dd* (6.2, 11.4)	

[a] Assignments confirmed by DQF-COSY, HSQC and HMBC experiments.

3.23 (1H, *t*, $J=8.7$ Hz), 3.45 (1H, *ddd*, $J=6.2$, 8.7 and 11.4 Hz), 3.85 (1H, *dd*, $J=6.2$ and 11.4 Hz), 4.15 (1H, *m*), 4.16 (1H, *d*, $J=7.3$ Hz) and 4.97 (1H, *d*, $J=5.9$ Hz) all ascribable to protons linked to oxygen bearing carbons. A DQF-COSY spectrum showed the sequence CH_2 (δ 2.82 and 2.87)-CHOH (δ 4.15)-CHOH (δ 4.97) attributable to the heterocyclic aliphatic ring of a flavonol (Bae et al., 1993) and the typical sequence of a β-D-xylopyranosyl residue (Table 1). In particular the *J* values of the signals ascribable to H-2 ($J=5.9$ Hz) and H-3 ($J=4.8$, 5.9 and 6.2 Hz) of the aglycone suggested at C-2 and C-3 the same stereochemistry as in catechin (Bae et al., 1993). A HSQC experiment, which correlated the proton resonances to the corresponding carbon signals as reported in Table 1, showed a glycosidation shift at C-3 (δ 76.9) of the aglycone (Agrawal, 1989), allowing us to deduce at this position the attachment of the β-D-xylopyranosyl unit. The HMBC spectrum, which showed the connectivities of the proton signals at δ 2.82 and 2.87 to C-10 (δ 112.4), C-5 (131.5), C-9 (δ 155.9), of the proton resonance at δ 4.15 to C-2 (δ 80.7) and of the signal at δ 4.97 to C-1′ (δ 132.2), C-2′ (δ 114.8) and C-6′ (δ 119.6), allowed the unambiguous assignment of the quaternary carbon resonances and confirmed the occurrence of the 3,3′,4′,7 tetrahydroxyflavan (fisetinidol) as the aglycone of **1** (Agrawal, 1989). A further correlation was observed between the anomeric proton signal at δ 4.16 and C-3 (δ 76.9) of fisetinidol. On the basis of the above data, **1** resulted to be the new fisetinidol-3-*O*-β-D-xylopyranoside, named anadanthoside.

It is to be noted that the occurrence of fisetinidol as the aglycone of a glycoside is a very unusual finding. Generally this flavanol is found in nature as monomer of dimeric proanthocyanidin (Nunes et al., 1989). The occurrence of dimeric flavan derivatives in the most polar extracts of the bark of *A. macrocarpa* will be the subject of further investigations.

2. Experimental

2.1. General

NMR spectra in CD_3OD were obtained using a Bruker DRX-600 spectrometer, operating at 599.19 MHz for ^1H and 150.86 MHz for ^{13}C. 2D experiments: ^1H-^1H DQF-COSY (Double Quantum Filtered Direct Chemical Shift Correlation Spectroscopy) (Bodenhausen, Freeman, Morrois, Neidermeyer, & Turner, 1977), inverse detected ^1H-^{13}C HSQC (Heteronuclear Single Quantum Coherence) (Bodenhausen & Ruben, 1980), HMBC (Heteronuclear Multiple Bond Connectivity) (Martin & Crouch, 1991). Optical rotations were measured on a Perkin-Elmer 141 polarimeter using a sodium lamp operating at 589 nm in 1% w/v solutions in MeOH. Fast atomic bombardment mass spectra (FABMS) were recorded in a glycerol matrix in the negative ion mode on a VG ZAB instrument (Xe atoms of energy of 2–6 KV).

2.2. Plant material

2.2.1. Anadenanthera macrocarpa

was collected at the Muchanes community (Alto Beni—North of La Paz, Bolivia) in September 1995 and identified by Lourdes Vargas and Rossy Michael (Herbario Nacional de Bolivia, Universidad Mayor de San Andrés).

A voucher sample is deposited at the National Herbarium in La Paz.

2.3. Isolation

The air-dried bark of *A. macrocarpa* (310 g) was defatted with petroleum ether (40–70°) and was successively extracted with $CHCl_3$ (1.4 g), $CHCl_3$/MeOH (9:1) (4.0 g) and MeOH (22 g). A portion of the $CHCl_3$/MeOH (9:1) residue (2.5 g) was chromatographed on a Sephadex LH-20 column (80 × 2 cm). Fractions (8 ml) were eluted with MeOH and checked by TLC on silica gel in $CHCl_3$–MeOH–H_2O (70:30:3). Fractions 58–63 (25 mg) contained pure **1**.

Compound **1**. $\alpha^{25}D+31.5$ (MeOH; c 0.1); FAB-MS

in negative ion mode: m/z 405 $[(M-H)]^-$, m/z 273 $[(M-H)-132]^-$. For ^1H and ^{13}C NMR: Table 1.

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Appendix

Anadanthoside: a new flavanol-3-*O*-β-D-xylopyranoside from *Anadenanthera macrocarpa*

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The new fisetinidol 3-*O*-β-D-xylopyranoside, named anadanthoside, was isolated from the bark of *Anadenanthera macrocarpa* (Leguminosae). The structure was assigned by FABMS and 2D NMR analysis.

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