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(−)-EPICATECHIN 5-*O*-β-D-XYLOPYRANOSIDE FROM *BROSIMOPSIS ACUTIFOLIUM*

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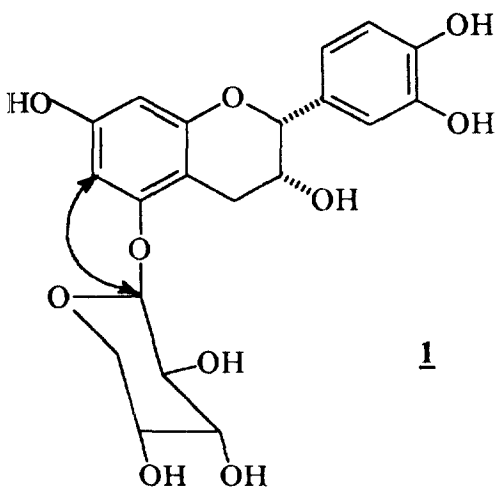
Key Word Index—*Brosimopsis acutifolium*; Moraceae; stem bark; (-)-epicatechin 5-*O*-β-D-xylopyranoside; NOE.

Abstract—In addition to 3,4-dihydroxybenzoic acid and (-)-epicatechin, a new glycoside of the latter has been isolated from the methanolic extract of the stem bark of *Brosimopsis acutifolium*. Its structure was established to be (−)-epicatechin 5-*O*-β-D-xylopyranoside on the basis of spectroscopic and chemical methods.

INTRODUCTION

In previous papers we have reported the isolation and characterization of a series of isoprenylated polyphenols from the root bark of *Brosimopsis oblongifolia* (Hub) Ducke [1–4]. In this communication we report the isolation and structure elucidation of a new compound **1** from stem bark of *B. acutifolium*, known in Brazil with the trivial name 'murure' [5], and used in traditional medicine as depurative, antirheumatic and for skin affections [6].



1

Fig. 1. Observed NOE is indicated by arrow

RESULTS AND DISCUSSION

Compound **1** was obtained as an amorphous laevorotatory powder. The unambiguous ^1H and ^{13}C NMR assignments are reported in Table 1, as a result of HETCOR and selective INEPT experiments. The ^1H NMR spectrum exhibited signals for five aromatic

Table 1. ^1H (300 MHz) and ^{13}C NMR (75 MHz) data for **1** in DMSO-d_6

	δ_H	δ_C
2	4.75 *br s*	78.45
3	3.98 *br s*	64.98
4	2.69 *d* (3.3 Hz)	28.48
4a	—	101.36
5	—	156.83
6	6.08 *d* (2.2 Hz)*	96.91
7	—	156.60
8	5.91 *d* (2.2 Hz)†	95.57
8a	—	155.72
1′	—	130.70
2′	6.90 *br s*	115.14[a]
3′	—	144.80[b]
4′	—	144.76[b]
5′	6.66 *br s*	115.09[a]
6′	6.66 *br s*	118.16
1″	4.68 *d* (7.41 Hz)	101.80
2″	3.20–3.70 *m*	73.40
3″	3.20–3.70 *m*	76.87
4″	3.20–3.70 *m*	69.65
5″	3.20–3.70 *m*	65.94

* INEPT long-range correlations with C-5, C-7 and C-4a.
† INEPT long-range correlations with C-7, C-8a and C-4a.
[a,b] Interchangeable.

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protons, two of which were *meta*-coupled (δ 5.91 and 6.08, $J = 2.2$ Hz), two broad 1H singlets (δ 4.75 and 3.98), the fifth a 2H doublet (δ 2.69, 3.3 Hz), suggesting the presence of an epicatechin unit in the molecule. In addition, the presence of a carbohydrate residue was indicated by the anomeric proton resonance at δ 4.68 (*d*, $J = 7.41$) and overlapping signals at δ 3.20–3.70. The ^{13}C NMR signals for the sugar were consistent with those of a xylopyranoside moiety. These findings were confirmed by enzymatic hydrolysis (see Experimental). The location of the sugar was fixed by the mutual enhancement of H-6 and H-1″ signals in the difference NOE experiments. On this basis **1** was assigned the structure of (−)-epicatechin 5-*O*-β-D-xylopyranoside.

EXPERIMENTAL

Plant material. Stem bark of *Brosimopsis acutifolium* (Hub) Ducke was obtained from Yerbalatina, Import–Export, Brazil.

Extraction and isolation. The Me_2CO-soluble portion (2 g) of the MeOH extract of the stem bark of *B. acutifolium* was chromatographed on silica gel ($CHCl_3$–Me OH–H_2O, 13:7:2; lower phase) to afford 3,4-hydroxybenzoic acid (100 mg), (−) epicatechin (50 mg) and **1** (mg 80).

(−)-*Epicatechin* 5-O-β-D-*xylopyranoside* (**1**). Amorphous powder. $[\alpha]_D - 55°$ (MeOH; *c* 0.30). ^1H NMR and ^{13}C NMR data (DMSO-d_6): see Table 1. ^1H NMR (C_5D_5N), δ: 3.28 (*dd*, $J = 4.4$ and 16.6 Hz, H-4a), 3.63 (*dd*, $J = 2.7$ and 16.6 Hz, H-4e), 4.0–4.5 (*m*, H2″-H5″), 4.58 *br t*, H-3), 5.22 (*br s*, H-2), 5.42 (*d*, $J = 7.3$, H-1″), 6.74 (*d*, $J = 2.3$ Hz, H-8), 7.04 (*d*, $J = 2.3$ Hz, H-6), 7.28 (*br s*, H-5′-H-6′), 7.88 (*br s*, H-2′); ^{13}C NMR (C_5D_5N), δ: 29.56 (C-4), 66.30 (C-3), 67.00 (C-5″), 70.71 (C-4″), 74.61 (C-2″), 78.67 (C-3″), 79.86 (C-2), 97.35 (C-8), 98.33 (C-6), 102.37 (C-4a), 103.50 (C-1″), 115.87/116.10 (C-2′, C-5′), 119.13 (C-6′), 131.76 (C-1′), 146.61/146.70 (C-3′, C-4′), 156.98/158.23/158.36 (C-5, C-7, C-8a).

Enzymatic hydrolysis of **1**. To a soln of **1** (30 mg) β-glycosidase (30 mg) was added. The mixt. was stirred for 3 days at room temp. and then extracted with EtOAc. The organic residue was purified on silica gel (EtOAc) to give (−) epicatechin identified by $[\alpha]_D$, co-TLC and ^1H NMR. The aq. phase was lyophilized and identified as xylose by co-TLC (*n*-BuOH–HOAc–H_2O; 4:1:5, upper phase).

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