Pergamon

PII: S0031-9422(97)00489-5

Phytochemistry, Vol. 46, No. 8, pp. 1451–1452, 1997

Printed in Great Britain
0031-9422/97 $17.00+0.00

TANNINS FROM *ALBIZIA LEBBEK*

YING-TSUN MA†, SHU-CHEN HSIAO, HSUE-FEN CHEN and FENG-LIN HSU*

† Department of Biochemistry, Taipei Medical College, Taipei, Taiwan, R.O.C.; School of Pharmacy, Taipei Medical College, Taipei, Taiwan 110, Republic of China

(*Received in revised form* 14 *March* 1997)

Key Word Index—*Albizia lebbek*; Leguminosae; bark; tannins; gentisic acid glycoside; syringic acid glycoside; albizinin; gentisic acid 5-*O*-[5-*O*-syringoyl-β-D-apiofuranosyl(1 → 2)]-β-D-glucopyranoside.

Abstract—A novel phenolic glycoside, albizinin, and four known flavan-3-ols, (−)-epicatechin, procyanidin B-2, procyanidin B-5 and procyanidin C-1, were isolated from the bark of *Albizia lebbek*. Structural elucidation was achieved by spectroscopic methods. © 1997 Elsevier Science Ltd

INTRODUCTION

Albizia lebbek has been used as a folk medicine in China for treating psychological disorders, insomnia and warts [1]. In other studies, the bark of this species was found to contain saponins and xanthones [2]. However, the tannin constituents still needed to be explored. The present paper describes the discovery of a new phenolic glycoside and four known tannins from the bark of *A. lebbek*.

RESULTS AND DISCUSSION

The aqueous acetone extract of the fresh bark of *A. lebbek* was repeatedly chromatographed on polystyrene and polydextran columns to yield (−)-epicatechin, procyanidin B-2, procyanidin B-5, procyanidin C-1 [3] and a phenolic compound (**1**). Compound **1**, an off-white amorphous powder, showed a blue-violet colour with $FeCl_3$ reagent. The $[M-H]^-$ at *m/z* 627 was in agreement with the molecular formula $C_{27}H_{17}O_{32}$. In the ^1H NMR spectrum of **1**, signals at δ 7.51 (1H, *d*, *J* = 3.0 Hz), 7.23 (1H, *dd*, *J* = 9.0, 3.0 Hz) and 6.73 (1H, *d*, *J* = 9.0 Hz), a set of signals for aromatic ABX-type protons, together with a signal of two aromatic protons at δ 7.26 (*s*), were observed . In addition, the ^1H NMR exhibited signals at δ 5.56–3.45 for two sugar moieties and at δ 3.86 (6H, *s*) for two methoxyl groups.

A DEPT experiment showed the presence of two carbonyl carbons (δ 166.4 and 172.2), two methoxyl carbons (δ 56.7), two aromatic rings and a five-carbon sugar, as well as a six-carbon sugar, in **1**. Detailed analyses of the ^1H-^1H COSY and ^1H-^{13}C COSY spectra led to assignment of the glycosidic moieties as apiofuranose [δ 68.1 (C-5), 75.1 (C-4), 78.4 (C-2), 78.7 (C-3) and 110.1 (C-1)], and glucopyranose [δ 62.4 (C-6), 71.4 (C-4), 77.4 (C-5), 77.7 (C-3), 78.3 (C-2) and 101.2 (C-1)].

The COLOC measurement of **1** showed ^3J interactions between H-6 (δ 7.51) and —COOH (δ 172.2), as well as H-6 and C-2 (δ 158.1), indicating that the carboxylic acid group at C-1 of the aromatic moiety is *ortho* to OH-2 and H-6, as in the case of gentisic acid glycoside [4]. On the other hand, a ^1H-^{13}C long-range correlation was observed between the signal of OCH_3 (δ 3.86, *s*, 6H) and the signals of C-3‴ and C-5‴ (δ 148.2, 2C) (Fig. 1), suggesting the presence of a syringic acid unit [5] in the aglycone.

The 2D NOESY indicated the proximity of glucose H-1 (δ 4.93, *d*, *J* = 7.4 Hz) with gentisic acid H-4 (δ 7.23, *dd*, *J* = 9.0, 3.0 Hz) and H-6 (δ 7.51, *d*, *J* = 3.0 Hz). Furthermore, the COLOC spectrum showed correlations between the H-5 (δ 4.40) of the apiose moiety and the COO— (δ 166.4) of the syringic acid unit.

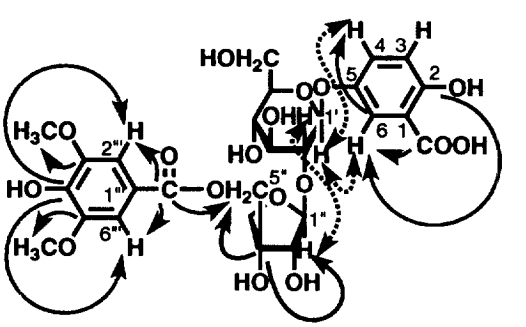

Fig. 1. COLOC (plain) and NOESY (dash) interactions of compound **1**.

* Author to whom correspondence should be addressed.

These correlations confirmed that the OH group at C-5 of gentisic acid was linked to the C-1 of glucose, whilst the syringic acid was substituted at C-5 of the apiose moiety. The apiosyl-(1 → 2)-glucosyl linkage of glycosidic moieties was assigned from the cross-peaks observed between apiose H-1 (δ 5.56, *d*, J = 1.0 Hz) and glucose H-2 (δ 3.69, *m*) in the NOESY. Also in the ^{13}C NMR spectrum of **1**, the position of the bond is confirmed by the chemical shift (δ 78.3) of glucose C-2, as compared with a non-substituted C-2, which is *ca* δ 72; the glycosidic signals were in good agreement with those of lignoids from Albiziae Cortex [6]. The β-configuration of C-1 in sugar moieties was determined based on the coupling constants (glucopyranose: 7.4 Hz; apiofuranose 1.0 Hz) of the anomeric protons [7]. Since only D-type is known for naturally occurring glucose and apiose, the component sugars in **1** were tentatively assigned to be D-type [8]. From the above results, the structure of **1** was determined to be gentisic acid 5-*O*-[5-*O*-syringoyl-β-D-apiofuranosyl(1 → 2)]-β-D-glucopyranoside and named albizinin.

EXPERIMENTAL

General. ^{1}H NMR 400 and ^{13}C NMR 100 Mz: acetone-d_6, with TMS as int. standard. CC: Sephadex LH-20 (Pharmacia), Cosmosil C-18-OPN (Nacalai), Diaion HP-20 and MCI gel CHP 20P (Mitsubishi Kasei).

Plant material. Fresh bark of *A. lebbek* (L.) Benth. was collected from the botanical garden of Taipei Medical College in November 1993. An appropriate voucher specimen is on deposit at this College.

Extraction and isolation. Fresh bark (14 kg) was extracted with 80% aq. Me_2CO at room temp., then concd *in vacuo*. The resulting residue was dissolved in H_2O, fractionated by CC on Diaion HP-20 and eluted with H_2O of increasing MeOH content, to afford frs I (10% MeOH) and II (30% MeOH). Fr. I was repeatedly chromatographed on Sephadex LH-20 (EtOH), MCI CHP 20P with a gradient mixt. of H_2O–MeOH (1:0 to 7:3) and Cosmosil C18-OPN (20% aq. MeOH) to provide (−)-epicatechin (12.24 g), procyanidin B-2 (4.73 g), procyanidin B-5 (920 mg) and procyanidin C-1 (4.42 g). Purification of fr. II by MCI CHP 20P with H_2O–MeOH (1:0 to 4:1), then by Cosmosil C18-OPN (15% aq. MeOH), yielded **1** (72.6 mg).

Albizinin (**1**). White amorphous powder. $[\alpha]_D^{26}$ −17.8° (Me_2CO; *c* 1.0). Negative FAB-MS *m/z* 627 $[M-H]^-$ (100). ^{1}H NMR (acetone-d_6): δ 3.49 (2H, *m*, glc H-4, 5), 3.69 (2H, *m*, glc H-2, 3), 3.72 (1H, *dd*, J = 12.4 and 4.5 Hz, glc H-6), 3.86 (6H, *s*, OCH_3), 3.87 (1H, *dd*, J = 12.4 and 2.2 Hz, H-6), 3.94 (1H, *d*, J = 9.6 Hz, api H-4), 4.12 (1H, *d*, J = 1.1 Hz, api H-2), 4.29 (1H, *d*, J = 9.6 Hz, api H-4), 4.38 (1H, *d*, J = 11.3 Hz, api H-5), 4.40 (1H, *d*, J = 11.3 Hz, api H-5), 4.93 (1H, *d*, J = 7.4 Hz, glc H-1), 5.56 (1H, *d*, J = 1.0 Hz, api H-1), 6.73 (1H, *d*, J = 9.0 Hz, H-3), 7.23 (1H, *dd*, J = 9.0 and 3.0 Hz, H-4), 7.26 (2H, *s*, H-2‴, 6‴), 7.51 (1H, *d*, J = 3.1 Hz, H-6). ^{13}C NMR (acetone-d_6): δ 56.7 (OCH_3), 62.4 (glc C-6), 68.1 (api C-5), 71.4 (glc C-4), 75.1 (api C-4), 77.4 (glc C-5), 77.7 (glc C-3), 78.3 (glc C-2), 78.4 (api C-2), 78.7 (api C-3), 101.2 (glc C-1), 108.2 (C-2‴, 6‴), 110.1 (api C-1), 112.9 (C-1), 117.9 (C-6), 118.6 (C-3), 121.0 (C-1‴), 126.3 (C-4), 141.8 (C-4‴), 148.2 (C-3‴, 5‴), 150.6 (C-5), 158.1 (C-2), 166.4 (C-7‴, —COO—), 172.2 (C-7, —COOH). Found: C, 46.7; H, 5.4. $C_{27}O_{17}H_{32}\cdot 7/2\ H_2O$ requires: C, 46.9; H, 5.7%).

Acknowledgements—We extend our appreciation to Mr Mu-Thun Kou (Taipei Medical College) for identification of plant material. Our sincere thanks to Ms Shou-Ling Huang (Taipei Regional Analytical Instrumentation Center, NSC) for measurements of the NMR spectra. This research was financially supported by the National Science Council of the Republic of China, grant NSC 85-2113-M-038-002.

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