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NOTE

Two new phenyl propanoid glycosides from the heartwood of *Cassia javanica*

Babita Agrawal* and J. Singh[a]

Chemistry Department, C.M.P. Degree College, Allahabad-211 002, Uttar Pradesh, India

E-mail : prashant_babita@yahoo.com

[a]Natural Product Laboratory, Department of Chemistry, University of Allahabad, Allahabad-211 002, Uttar Pradesh, India

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Abstract : Two new glycosides, 4-hydroxycinnamyl alcohol-4-*O*-β-D-glucopyranoside and 4-hydroxy-3-methoxycinnamyl alcohol-4-*O*-β-D-glucopyranoside, were isolated from the heartwood of *Cassia javanica*. The structures were established on the basis of chemical evidences and spectroscopic methods specially ^{13}C and ^{1}H NMR.

Keywords : *Cassia javanica*, Leguminosae, phenyl propanoid, 4-hydroxycinnamyl alcohol-4-*O*-β-D-glucopyranoside, 4-hydroxy-3-methoxycinnamyl alcohol-4-*O*-β-D-glucopyranoside.

Introduction

Cassia species are rich in flavonoids, anthocyanidins, anthraquinones and polysaccharides. *Cassia javanica* is reported in Indian system of medicine[1], therefore we undertook the systematic chemical study of constituents of heartwood of this species. We report herein the isolation and characterization of two new phenyl propanoid glycosides. No phenyl propanoids have so far been reported from any species of *Cassia*. The phenyl propanoids reported in the paper are novel findings in the natural products.

Results and discussion

Crushed and air-dried heartwood were extracted with ethanol and the extract directly analysed by TLC, flash CC and prep. TLC of the hexane soluble portion of the ethanolic extract, yielded compounds **1** and **2**.

Compound **1**, $C_{15}H_{20}O_7$ ($[M]^+$, *m/z* 312), m.p. 171-174 °C was a glycoside. Its IR spectrum showed hydroxyl absorption at 3400 cm^{-1}, peak at 970 cm^{-1} was characteristic for *trans* C=C and peaks at 1500-1600 cm^{-1} due to an aromatic ring. ^{1}H NMR spectrum showed an anomeric proton signal at δ 4.85 (1H, d, *J* 7.1 Hz) and was consistent with the configuration of β-D-glucose. On acid hydrolysis, **1** afforded 4-hydroxycinnamyl alcohol, identified by ^{1}H and ^{13}C NMR spectra[2,5] and the sugar, β-D-glucose identified by PC and GC of their TMS derivative.

The position of attachment of glucose on the aglycone was established with the help of ^{13}C NMR spectrum. Comparison of the ^{13}C NMR spectra of 4-hydroxycinnamyl alcohol and its glycoside **1** demonstrated that effects of glycosylation are quite unusual in this type of compounds. C-4 glucosylation led to a small downfield shift of 2.6 ppm to δ 157.0 for C-4, but not upfield as usually observed in polyphenols[3]. Carbons *ortho* (C-3 and C-5) and *para* (C-1) undergo usual downfields shifts of 2.4 and 1 8 ppm, respectively, as compared to 4-hydroxycinnamyl alcohol. On the other hand, examination of the ^{1}H NMR spectrum of **1** shows that all aromatic protons move downfield as compared to 4-hydroxycinnamyl alcohol H-3 and H-5 being more affected (0.28 ppm) than H-2 and H-6 (0.22 ppm)[4], confirming the attachment of glucose to the phenolic hydroxyl group.

Thus compound **1** was characterized as 4-hydroxycinnamyl alcohol-4-*O*-β-D-glucopyranoside.

Compound **2**, $C_{16}H_{22}O_8$ ($[M]^+$*m/z* 3420), m.p. 158 °C was also a glycoside. The ^{13}C NMR spectrum of **2** showed the presence of carbohydrate signals at similar chemical shifts as for **1** demonstrated that this compound is also a monoglucoside. The ^{1}H NMR signal of anomeric proton (δ 4.40, 1H, d, *J* 7.3 Hz) confirmed the presence

of a β-D-glucose moiety. A singlet at δ 3.75 in ^{1}H NMR spectrum confirmed the presence of a methoxyl group.

The ^{13}C NMR spectrum showed the presence of a methylene carbon atom at δ 62.0 and two sp^2 carbon signals at δ 129.2 and 129 in addition to aromatic carbon signals, suggesting that **2** had a *trans* double bond in a side chain[5]. The splitting pattern observed for the protons at δ 6.08, 6.38 and 4.28 in the ^{1}H NMR spectrum is typical of aromatic propen-2-yl alcohol side chain[2] identical to that of compound **1** side chain, suggesting that the aglycone signals were similar in the ^{13}C NMR spectra of **2** and **1**, except for aromatic carbons. The ^{1}H NMR spectrum demonstrated the presence of three aromatic protons in the form of one double doublet (J_{ortho} 8 Hz and J_{meta} 2 Hz) and of 2 doublets (J_{ortho} for the first and J_{meta} for the second). This established the aromatic ring as 1,3,4-trisubstituted[4]. Thus compound **2** has one methoxyl group at C-3 of aromatic ring which is not present in compound **1**. The position of attachment of glucose to the aglycone was C-4, confirmed by ^{1}H and ^{13}C NMR spectra showing similar glycosylation shifts as compound **1**.

Thus, compound **2** was characterized as 4-hydroxy-3-methoxycinnamyl alcohol-4-*O*-β-D-glucopyranoside.

Experimental

M.p.s are uncorrected. TLC was carried out on silica gel G. Prep. TLC and flash CC was also done on silica gel G. ^{1}H NMR spectra were recorded on 90 MHz Perkin-Elmer R-32 NMR instrument in $CDCl_3$ and $(CD_3)_2CO$ solution using TMS as internal standard, IR as KBr disks on Perkin-Elmer 297 spectrophotometer.

Plant material : Heartwood of *Cassia javanica* was collected in Allahabad, India. A voucher specimen was deposited in the Botanical Survey of India, Allahabad, India.

Extraction and isolation : Air-dried material was ground and extracted with EtOH for two weeks. The extract was concentrated and poured into water, separating into water soluble and insoluble fractions. Hexane soluble portions of the water insoluble fraction were loaded on to a flash column and eluted with solvents increasing polarity. Elution with $CHCl_3$-EtOAc (1 : 1) yielded a fraction containing mixture of compounds (**1** and **2**). These compounds were separated by prep. TLC. Both compounds were recrystallized from $CHCl_3$.

Compound **1** : White granular compound, m.p. 171 °C (Found : C, 57.70; H, 6.43. Calcd. for $C_{15}H_{20}O_7$: C, 57.69, H, 6.41%); IR (KBr) : 3400, 1603, 1518, 970 cm^{-1}; ^{1}H NMR : δ 4.85 (1H, d, *J* 7.1 Hz, C-1-H of glucose), 6.98 (2H, dd, *J* 8.5 and 2 Hz, H-2 and H-6), 7.35 (2H, dd, *J* 8.5 and 3 Hz, H-3 and H-5), 6.49 (1H, d, *J* 16 Hz, H-7), 6.24 (1H, dt, *J* 5.1 and 16.0 Hz, H-8), 4.09 (2H, t, *J* 5.1 Hz, 9-CH_2); ^{13}C NMR : δ 131.8 (C-1), 127.8 (C-2), 117.7 (C-3), 157.0 (C-4), 117.7 (C-5), 127.8 (C-6), 129.6 (C-7), 129.0 (C-8), 62.3 (C-9); Glc 102.0 (C-1), 74.8 (C-2), 78.3 (C-3), 71.2 (C-4), 78.7 (C-5), 62.9 (C-6).

Compound **2** : White amorphous powder; m.p. 158 °C (Found : C, 56.12; H, 6.44. Calcd. for $C_{16}H_{22}O_8$: C, 56.14; H, 6.42%); IR (KBr) : 3400, 2885, 1610, 1600, 1520, 1500, 1190, 970 cm^{-1}; ^{1}H NMR : δ 3.75 (3H, s, -OCH_3), 4.90 (1H, d, *J* 7.3 Hz, C-1-H of glucose), 3.5–3.7 (m, sugar proton), 7.10 (1H, d, *J* 2 Hz, H-2), 7.48 (1H, d, *J* 8 Hz, H-5), 6.95 (1H, dd, *J* 2 and 8 Hz, H-6), 6.38 (1H, d, *J* 16 Hz, H-7), 6.08 (1H, dq, *J* 6 and 16 Hz, H-8), 4.28 (2H, d, *J* 5.6 Hz, 9-CH_2); ^{13}C NMR : δ 133.7 (C-1), 111.5 (C-2), 150.5 (C-3), 148.0 (C-4), 118.0 (C-5), 120.7 (C-6), 129.2 (C-7), 129.0 (C-8), 62.0 (C-9), 56.5 (-OCH_3); Glc 102.0 (C-1), 74.8 (C-2), 78.3 (C.3), 71.2 (C-4), 77.9 (C-5), 62.2 (C-6).

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