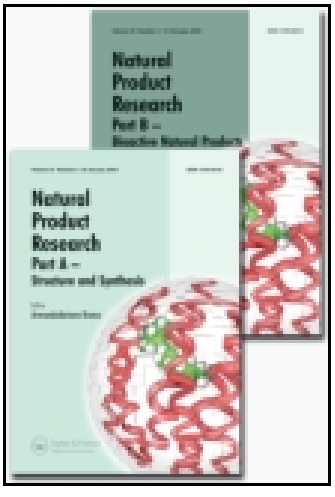

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(2-Nitro ethyl)phenyl and cyanophenyl glycosides from the fruits of *Diploclisia glaucescens*

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Chemical investigation of polar fractions of the methanol extract of the fruits of *Diploclisia glaucescens* of the family Menispermaceae furnished two new phenyl glycosides, 4-(2-nitroethyl)phenyl-β-D-xylopyranosyl-(1$\sim$6)-β-D-glucopyranoside, and 4-cyanophenyl-β-D-xylopyranosyl-(1$\sim$6)-β-D-glucopyranoside.

Keywords: Diploclisia glaucescens; Menispermaceae; (2-Nitro ethyl)phenyl glycosides; Cyanophenyl glycosides

1. Introduction

Diploclisia glaucescens of the family Menispermaceae is a liana growing in the mid-country regions of India and Sri Lanka. Leaves of the plant have been used in the treatment of biliousness and venereal diseases [1]. It is a rich source of phytoecdysteroids and triterpenoidal saponins. Several phytoecdysteroids, saponins, triterpenoids and alkaloids have been reported from the seeds, leaves, stem and fruits of the plant [2–13]. We have recently reported the isolation of a new ecdysteroid 2-deoxy-5,β,20-dihydroxyecdysone, together with 20-hydroxyecdysone, 3-deoxy-l,β, 20-dihydroxyecdysone, 2-deoxy-20-hydroxyecdysone, 24-ethyl-20-hydroxyecdysone (makisterone C, lemmasterone, podecdysone) from the ethyl acetate extract [6] and some triterpenoidal and steroidal saponins from the fruits of the plant [12,13]. In this article, we report the isolation of two new phenyl glycosides, 4-(2-nitro ethyl)phenyl-β-D-xylopyranosyl-(1$\rightarrow$6)-β-D-glucopyranoside (**1**), and 4-cyanophenyl-β-D-xylopyranosyl-(1$\rightarrow$6)-β-D-glucopyranoside (**2**) from the methanol extract of the fruits of *D. glaucescens*.

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Dedicated to Prof. G. P. Wannigama on the occasion of his 77th birthday.

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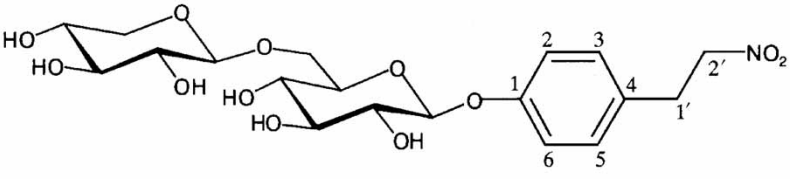
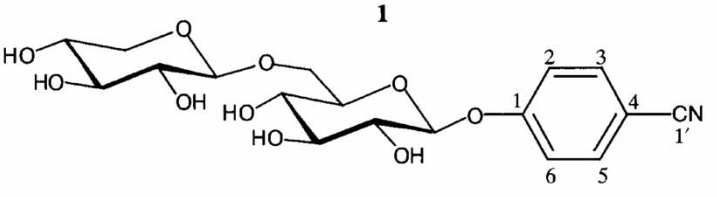
2. Results and discussion

In order to study about high polar compounds, the methanol extract was chromatographed over silica gel with EtOAc–MeOH. The column fractions, which contained UV active spots on thin layer chromatography (TLC), were combined and passed through the reversed phase high performance liquid chromatography (HPLC). Purification of the fraction eluted with 70% H_2O–MeOH, furnished two phenyl glycosides (**1**) and (**2**).



1



2

The compound **1** was obtained as colorless needles. Acid hydrolysis of **1** with 4 N HCl gave D-xylose and D-glucose as the only sugar moieties present in compound **1**. The peaks observed in the IR spectrum at V_{max} 1547 and 1381 cm^{-1} suggested the presence of an aliphatic nitro group in the compound **1**. The positive ion FABMS of compound **1** displayed a peak at m/z 484 which has been assigned to $[M + Na]^+$, suggesting the molecular weight of compound **1** to be 461. The HRFABMS of **1** observed at m/z 484.1446 ($C_{19}H_{27}O_{12}NNA$ requires 484.1431), suggested the molecular formula of **1** to be $C_{19}H_{27}O_{12}N$. The ^{13}C NMR of **1** indicated the presence of 19C in the molecule and the DEPT spectrum suggested the presence of 2 quaternary carbons, 4 methylene carbons and 13 methine carbons in compound **1**. The two *ortho*-coupled doublets observed at δ7.17 ($J = 8.7$ Hz) and 7.06 ($J = 8.7$ Hz) indicated the presence of *para*-substituted aromatic ring in the molecule. In accordance with this, two quaternary carbons were observed at δ131.6 and 158.0, besides two duplicated CH carbons at δ118.0 and 130.8. The δ158.0 signal could be assignable to an oxygenated aromatic carbon, while the δ131.6 signal to an alkyl substituted aromatic carbon. The ^1H NMR spectrum showed two anomeric doublets at δ4.86 and 4.31 indicating the presence of two sugar moieties in the compound **1**. This was further supported by the two carbon signals observed at δ102.1 and 105.2. Irradiation of the anomeric signal observed at δ4.86 (H-1 of g1c) enhanced the peak (δ7.06) of the benzene ring, indicating the linkage of glucopyranosyl group and benzene ring. Irradiation of the anomeric signal at δ4.31 of xylopyranosyl moiety enhanced the two doublets at δ3.78 and 4.09, which were assigned for H-6 of glucopyranosyl moiety. These observations revealed that a disaccharide moiety, β-D-xylopyranosyl-(1 ~ 6)-*p*-D-glucopyranosyloxy group, is attached to the benzene ring. The remaining two CH_2 carbons observed at δ_C 33.5 (δ_H 3.21), δ_C77.5 (δ_H 4.67) were assigned as C-1 and C-2 of a 2-nitro ethyl group, respectively, attached to

Table 1. ^{13}C and ^{1}H NMR (125 MHz and 500 MHz, CD_3OD) data of compounds **1** and **2**.

	1		**2**	
C. No.	^{13}C	^{1}H	^{13}C	^{1}H
1	158.0	–	162.3	
2/6	118.0	7.06 (d, 8.7)	118.5	7.26 (d, 8.9)
3/5	130.8	7.17 (d, 8.7)	135.2	7.68 (d, 8.9)
4	131.6	–	106.4	
l′	33.5	3.21 (t, 7.2)	119.9	
2′	77.5	4.67 (t, 7.2)	–	
g1c-l	102.1	4.86 (d, 8.4)	101.6	4.97 (d, 8.0)
g1c-2	74.8	3.47 (dd, 10.2, 8.4)	75.0	3.47 (dd, 10.1, 8.0)
g1c-3	77.7	3.48 (t, 10.2)	77.7	3.48 (t, 10.1)
g1c-4	71.4	3.38 (m)	71.3	3.35 (m)
g1c-5	77.3	3.63 (ddd, 9.8, 6.3, 1.9)	77.7	3.70 (ddd, 9.0, 6.8, 1.4)
g1c-6	69.7	3.78 (dd, 11.8, 6.3)	69.9	3.74 (dd, 11.1, 6.8)
		4.09 (dd, 11.8, 1.9)		4.12 (brd, 11.1)
xyl-l	105.2	4.31 (d,7.5)	105.5	4.29 (d, 7.5)
xyl-2	74.8	3.20 (dd, 9.0, 7.5)	75.0	3.19 (dd, 8.9, 7.5)
xyl-3	77.7	3.27 (t, 8.9)	77.6	3.25 (t, 8.9)
xyl-4	71.1	3.45 (ddd, 10.3, 8.9, 5.3)	71.2	3.44 (ddd, 10.3, 8.8, 5.2)
xyl-5	66.8	3.09 (dd, 11.5, 10.3)	66.9	3.11 (dd, 11.4, 10.3)
		3.82 (dd, 11.5, 5.3)		3.82 (dd, 11.4, 5.2)

J values are expressed in Hz.

the phenyl group. Hence, the structure of **1** was unambiguously established as a new natural product 4-(2-nitro ethyl)phenyl-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside. Compound **1** is regarded as a 6′-O-β-D-xylopyranosyl derivative of thalictoside [4-(2-nitro ethyl)phenyl-β-D-glucopyranoside] [14].

Compound **2** was obtained as a sticky solid. Acid hydrolysis of **2** also gave D-xylose and D-glucose as the sugar moieties. The positive mode FABMS showed a peak at m/z 436 for $[M+Na]^+$ indicating the molecular formula of compound **2** to be $C_{18}H_{23}O_{10}N$. Comparison of the ^{1}H and ^{13}C NMR of **2** with those of **1** revealed that compound **2** has a β-substituted benzene ring and the same disaccharide moiety attached to the benzene ring, as in **1**. A quaternary carbon signal was observed at δ119.9 in the ^{13}C NMR spectrum of **2**, instead of an ethylene group of **1**. This carbon signal was assigned to that of a CN group, and the presence of a nitrile group was confirmed by the IR absorption at 2230 cm^{-1}. Hence, the structure of **2** was determined to be a new natural product, 4-cyanophenyl-β-D-xylopyranosyl-(l → 6)-β-D-glucopyranoside. Table 1 lists the complete ^{1}H and ^{13}C assignments of compounds **1** and **2**.

3. Experimental

3.1. *General*

Melting points were determined by Gallenkamp apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-360 polarimeter at 25°C. UV spectra were recorded on a UV-160 A spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX500 (500 MHz for ^{1}H and 125 MHz for ^{13}C) spectrometer in CD_3OD solution. The signal of residual protium of the solvent ($\delta = 3.30$) was used as a reference for ^{1}H chemical shifts, while CD_3OD signal ($\delta = 49.0$) was used as a

reference for ^{13}C-chemical shifts. Positive ion FABMS were obtained on a JEOL JMS-AX505HA spectrometer with glycerol as matrix. HPLC analyses were carried out on Shimadzu LC-6A apparatus equipped with a UV detector under reversed phase C_{18} and isocratic solvent conditions.

3.2. *Plant material*

The unripe fruits of *D. glaucescens* were collected from the central province of Sri Lanka in April 2001. A voucher specimen is deposited at the Institute of Fundamental Studies.

3.3. *Extraction and isolation*

The dried unripe, ground fruits of *D. glaucescens* (800 g) were defatted with *n*-hexane and extracted with ethyl acetate and then methanol. Evaporation of methanol gave brown solid (110 g). A portion of methanol extract (80 g) was chromatographed over silica gel (Merck Art. 7734) with EtOAc–MeOH. The column fractions, which contained UV active spots on TLC, were combined (22 g). A portion (15 g) of the fraction was passed through the preparative HPLC (STR Prep-ODS, 20×250 mm column; 6 mL min^{-1}; 70% H_2O–MeOH to 100% MeOH; UV detection 243 nm). The fraction eluted with 70% H_2O–MeOH were evaporated to dryness (970 mg) and separated with the same HPLC column with 75% H_2O–MeOH as an eluent to give compounds **1** (13 mg) and **2** (148 mg).

4-(2-Nitro ethyl)phenyl-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside (1). M.p. 122–124°C; IR V_{max} (KBr): 1547, 1381 cm^{-1}; ^1H NMR and ^{13}C NMR: see table 1; FABMS(+): m/z 484 $[M + Na]^+$; HRFABMS(+): m/z 484.1446 ($C_{19}H_{27}O_{12}NNa$ requires 484.1431).

4-Cyanophenyl-β-D-xylopyranosyl-(1 → 6)-β-D-glucopyranoside (2). Amorphous solid; IR V_{max} (KBr): 2230 cm^{-1}; FABMS(+): m/z 436 $[M + Na]^+$; HRFABMS(+): m/z 436.1247 ($C_{18}H_{23}O_{10}NNa$ requires 436.1247).

References

[1] R.N. Chopra, S.L. Nayar, I.C. Chopra. *Glossary of Indian Medicinal Plants*, pp. 72–99, Council of Scientific and Industrial Research, New Delhi (1956).
[2] R.W. Miller, J. Clardy, J. Kozlowski, K.L. Mikolajczak, R.D. Plattner, R.G. Powell, C.R. Smith, D. Weisleder, Q-T. Zheng. *Planta Med.*, **51**, 40 (1985).
[3] B.M.R. Bandara, L. Jayasinghe, V. Karunaratne, G.P. Wannigama, M. Bokel, W. Kraus, S. Sotheeswaran. *Phytochemistry*, **28**, 1073 (1989).
[4] L. Jayasinghe, C.P. Jayasooriya, K. Oyama, Y. Fujimoto. *Steroids*, **67**, 555558 (2002).
[5] L. Jayasinghe, C.P. Jayasooriya, N. Hara, Y. Fujimoto. *Tetrahed. Lett.*, **44**, 8769 (2003).
[6] L. Jayasinghe, B.M.M. Kumarihamy, B.G.S. Arundathie, L. Dissanayake, N. Hara, Y. Fujimoto. *Steroids*, **68**, 447 (2003).
[7] D.L.B. Jayasinghe, G.P. Wannigama, J.K. MacLeod. *J. Chem. Soc. Pak.*, **20**, 131 (1998).
[8] U.L.B. Jayasinghe, G.P. Wannigama, J.K. MacLeod. *Nat. Prod. Lett.*, **2**, 249 (1993).

[9] U.L.B. Jayasinghe, G.P. Wannigama, S. Balasubramaniam, H. Nasir, Atta-ur Rahman. *J. Nat. Sci. Council Sri Lanka*, **20**, 187 (1992).
[10] B.M.K. Bandara, D.L.B. Jayasinghe, V. Karunaratne, G.P. Wannigama, M. Bokel, W. Kraus, S. Sotheeswaran. *Planta Med.*, **56**, 290 (1990).
[11] B.M.K. Bandara, L. Jayasinghe, V. Karunaratne, G.P. Wannigama, W. Kraus, M. Bokel, S. Sotheeswaran. *Phytochemistry*, **28**, 2783 (1989).
[12] U.L.B. Jayasinghe, B.A.L.S. Balasooriya, N. Hara, Y. Fujimoto. *Nat. Prod. Res.*, **19**, 245 (2005).
[13] L. Jayasinghe, N. Hara, Y. Fujimoto. *Phytochemistry*, **62**, 563 (2003).
[14] H. lida, T. Kikuchi, K. Kobayashi, H. Ina. *Tetrahed. Lett.*, **21**, 759 (1980).