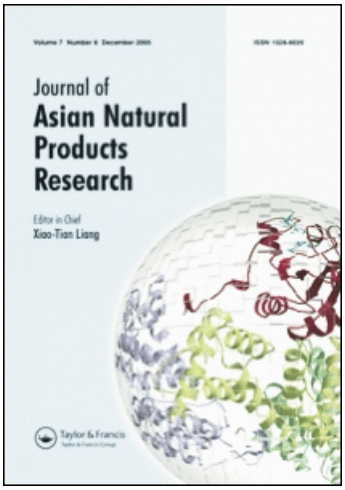

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Two new lignan glycosides from *Trachelospermum lucidum* (D. Don) Schum

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Two new lignans (**1** and **2**) having a diarylhydroxybutyrolactone skeleton were isolated from the leaves of *Trachelospermum lucidum* (D. Don) Schum. Their structures were elucidated to be apocynotrachelolegnin 5′-*O*-β-D-glucopyranoside (**1**) and rafanotrachelogenin 4-*O*-β-D-glucopyranoside (**2**) on the basis of spectroscopic analysis. Two known lignans, matairesionoside-4-*O*-β-D-glucoside (**3**) and trachelosiaside (**4**), were also isolated from *Trachelospermum lucidum*.

Keywords: *Trachelospermum lucidum* (D. Don) schum; apocynotrachelolegnin; rafanotrachelogenin; apocynaceae

1. Introduction

The genus *Trachelospermum* (Apocynaceae) comprises 30 species distributed mainly in India, Japan and the United States. In Pakistan, only two species, *T. lucidum* and *T. jasminoides*, are found. *Trachelospermum lucidum*, locally called Dudhi, occurs from Rawalpindi to Abbotabad. The plant is suitable for covering embankments and prefers moist and shady places; its milky juice is applied to ulcers. The plant is similar to *Alstonia scholaris* whose bark is bitter, tonic and useful in malaria, diarrhoea, dysentery and snake bite.[1] Previous studies revealed a number of flavonoids,[2] lignans[3] and alkaloids.[4] At present we are reporting the isolation and structure elucidation of new compounds **1** and **2**.

2. Results and discussion

From the butanolic fraction of *T. lucidum* (D. Don) Schum, compound **1** was isolated. The molecular formula for **1** was assigned as $C_{26}H_{32}O_{11}$ from HRFAB–MS at *m/z* 543.1880 and the quasi-molecular ion peaks at *m/z* 543 ($[M + Na]^+$), 559 ($[M + K]^+$) in FAB–MS. The IR spectrum revealed the presence of hydroxyl groups (3507 cm^{-1}) and a lactone ring (1735 cm^{-1}). The carbons resonating at δ 102.9 (C-1), δ 74.9 (C-2), δ 77.8 (C-3), δ 71.3 (C-4), δ 78.1 (C-5), δ 62.5 (C-6) and an anomeric proton signal at δ 4.85 (1H, d, $J = 8.0$ Hz, H-1″) indicated the presence of a β-glucopyranosyl.[5] In addition to those protons attributed to glucose, the ^{1}H NMR spectrum (Table 1) showed signals due to two substituted aromatic rings at δ 6.66 (d, $J = 1.6$ Hz, H-2), δ 6.57 (dd, $J = 1.6$ Hz, H-2′), δ 7.05 (d, $J = 1.5$ Hz, H-4′), δ 6.50 (d, $J = 8.0$ Hz, H-5), δ 6.75 (dd, $J = 8.0$, 1.6 Hz, H-6), δ 6.49 (d, $J = 1.4$ Hz, H-6′), respectively. In the ^{1}H NMR spectrum, signals for the methylene protons of lactone moiety were δ 4.10 dd (1H, d, $J = 13.4$, 6.6 Hz, H-9′) and 4.10 (1H, dd, $J = 13.4$, 6.6 Hz, H-9′). Another AB-type CH_2 showed its proton signals in ^{1}H NMR spectrum at δ 2.54 (1H, dd, $J = 11.9$, 6.1 Hz, H-7) and 2.89 (1H, dd, $J = 11.9$, 4.1 Hz, H-7), respectively. The ^{13}C NMR DEPT and ^{1}H NMR spectra of **1** (Figures 1 and 2) indicated the presence of two methoxy groups at δ 3.78 (3H, s, H-3′a) and 3.81 (3H, s, H-4a) and one phenolic hydroxyl at δ 8.71 (1H, s) was also present. The above evidence demonstrated a diarylhydroxybutyrolactone lignan for the aglycone moiety of **1**.[6–7] The ^{13}C NMR spectra of **1** (Table 1) displayed 20 carbon signals for the aglycone moiety, which were almost identical with those of trachelosiaside (**4**). The HMBC correlation between the anomeric proton at δ 4.85 and C-5′ (δ 150.7), with a relatively downfield chemical shift, firmly demonstrated the glucosyl linkage to C-5′. From the above evidences compound **1** has been determined as apocynotrachelolegnin 5′-*O*-β-D-glucopyranoside. The FAB–MS of compound **2** showed pseudomolecular quasi-ion peaks at *m/z* 573 $[M + Na]^+$, 589 $[M + K]^+$. The ^{1}H NMR spectrum (Table 1) showed three downfield singlets for the methoxy groups at δ 3.47, 3.48 and δ 3.78 respectively, and was confirmed by ^{13}C NMR DEPT spectrum of compound **2** in Figure 3. A downfield proton of aglycone moiety showed its signal at δ 5.19 (1H, dd, $J = 7.0$ Hz, H-5) in ^{1}H NMR spectrum. Two downfield

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Table 1. ^{1}H NMR and ^{13}C NMR spectral data for **1** and **2** in (CD_3OD 500/125 MHz in ppm).

	1			**2**	
No.	^{1}H (*J* in Hz)	^{13}C	No.	^{1}H (*J* in Hz)	^{13}C
1	–	130.3	1	–	131.3
2	6.66 d (1.6)	114.8	2	6.53 d (2.3)	113.1
3	–	146.2	3	–	146.2
3-OH	8.71 broad s	–	3-a	3.47 s	56.4
4	–	144.0	4	–	150.6
4-a	3.78 s	56.7	5	6.49 d (8.1)	122.2
5	6.50 d (8.0)	116.2	6	6.69 dd (2.0, 7.8)	116.2
6	6.75 dd (8.0, 1.6)	115.0	7	2.71 dd (13.4, 6.4)	
				2.91 dd (13.4, 4.2)	35.1
7	2.54 dd (11.9, 6.1), 2.89 dd (11.9, 4.1)	35.3	8	2.31 m	47.7
8	2.45 m	42.5	9	–	181.6
9	–	181.4	1′	–	134.3
1′	–	135.1	2′	6.64 d (1.7)	123.1
2′	6.57 d (1.6)	113.3	3′	–	146.8
3′	–	147.0	3′-a	3.48 s	65.7
3′-a	3.81 s	56.4	4′	–	149.0
4′	7.05 d (1.5)	118.0	4′-a	3.78 s	57.7
5′	–	150.7	5′	6.69 d (7.0)	116.2
6′	6.49 d (1.6)	122.2	6′	7.0 dd (2.0, 7.4)	
7′	2.41 dd (10.1, 4.3)	39.0	7′	5.19 d (7.0)	82.8
8′	2.70 m	47.6	8′	2.73 m	42.7
9′	4.10 dd (13.4, 6.6)	73.0	9′	4.17 dd (12.0, 4.0)	72.7
1″	4.85 d (7.4)	103.0	1″	4.87 d (8.1)	102.1
2″	4.49 d (7.4)	75.0	2″	3.31 d (7.8)	73.2
3″	3.30 t (7.4)	78.0	3″	3.39 t (7.8)	77.7
4″	4.41 t (7.8)	71.3	4″	3.49 t (7.8)	78.1
5″	3.89 ddd (12.0, 1.7, 8.0)	78.1	5″	3.34 ddd 1.7, 7.8, 10.8)	78.1
6″	3.31 dd (1.7, 12.0)	62.5	6″	3.59 dd (1.7, 11.0)	62.4
	3.59 dd (7.8, 12.0)			3.62 dd (1.8, 10.5)	

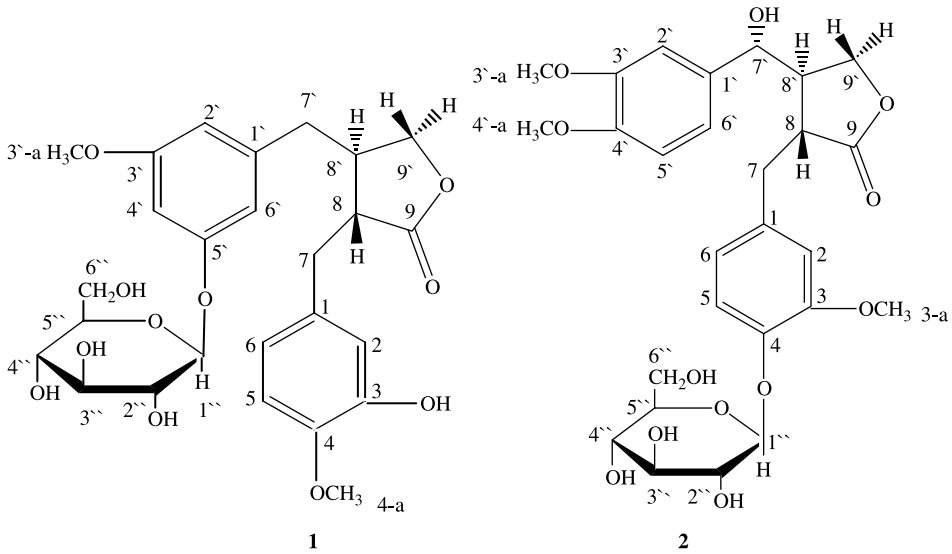

Figure 1. Structures of compounds **1** and **2**.

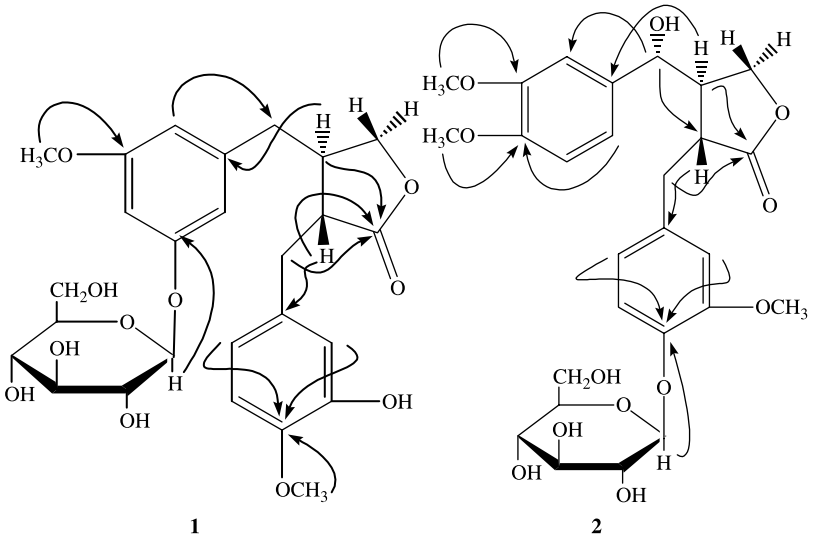

Figure 2. Selective HMBC correlations of **1** and **2**.

protons at δ 3.89 (t, 11.9 Hz, H-9′) and 4.17 (dd, 11.9, 4.0 Hz, H-9′) were for the methylene of lactone moiety. Two substituted aromatic rings disclosed six proton signals in ^{1}H NMR spectrum at δ 6.53 (1H, d, $J = 2.3$ Hz, H-2), 6.64 (1H, d, $J = 1.7$ Hz, H-2′), 6.49 (1H, d, $J = 8.1$ Hz, H-5), 6.69 (d, $J = 7.0$ Hz, H-5′), 6.75 (dd, $J = 8.1, 2.3$ Hz, H-6), and 7.08 (dd, $J = 7.0, 1.7$ Hz, H-6′), respectively. The ^{13}C NMR spectrum confirmed the presence of carbonyl group of lactone ring at δ 181.6. In the HMBC spectrum the cross peak between this carbonyl of lactone moiety with the proton (H-8′) confirmed the linkage. The ^{1}H NMR and ^{13}C NMR spectra (Table 1) of **2** indicated the presence of lignan aglycone, and a β-glycosyl moiety which was also affirmed by the 2D NMR spectra of **2** (^{1}H–^{1}H COSY, HMQC, HMBC and NOESY). The anomeric proton of β-glycosyl moiety appeared at δ 4.87 (1H, d, $J = 8.1$ Hz, H-1″),[8] which was attributed using an HMQC experiment to a carbon at δ 102.1.[9] The ^{1}H–^{1}H COSY spectrum showed the glycosidic chain and HMQC disclosed that other sugar carbon atoms resonated at δ 62–78. The hexose was identified as β-glucopyranose on the basis of its ^{1}H NMR and ^{13}C NMR spectral data.[10] The HMBC correlation between the anomeric proton of this glucosyl and C-4 in the lignan moiety substantiated the linkage position. From the above evidence **2** was determined as rafanotrachelogenin 4-*O*-β-D-glucopyranoside. Compounds **3** and **4** were determined as matairesionoside-4-*O*-β-D-glucoside and trachelosiaside, respectively.

3. Experimental

3.1 General experimental procedures

Optical rotations were measured using a Jasco-DIP-360 digital polarimeter. UV and IR spectra were recorded on Htichi-UV-3200 and Jasco-320-A spectrophotometer, respectively. ^{1}H NMR and ^{13}C NMR, COSY, HMQC and HMBC spectra were performed on Bruker

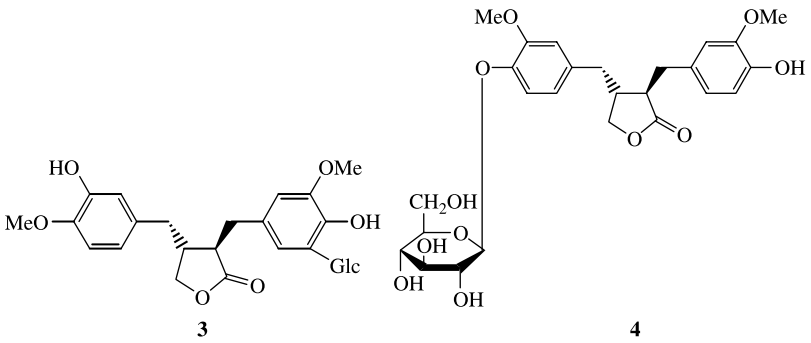

Figure 3. Structures of compounds **3** and **4**.

spectrometers operating at 500 and 400 MHz, chemical shifts in ppm and coupling constants were in Hz. EI–MS was obtained from JMS HX-110 with a data system. Column chromatography (CC) was performed by using silica gel, 70–230 mesh. Flash chromatography (FC) was carried-out by using silica gel, 230–400 mesh. The detection of the isolated compounds was carried out using TLC: pre-coated silica gel G-25-UV_{254} plates, UV lamp operating at 254 nm and by spraying with ceric sulphate.

3.2 Plant material

The aerial parts of *Trachelospermum lucidum* (D. Don) Schum were collected from Mountain Eelum in Swat, Pakistan in July 2003. Taxonomic identification was done by Dr Habib Ahmad (taxonomist), Department of Botany, Postgraduate Jahan Zeb College, Saidu Sharif, Swat, Pakistan. A voucher specimen (# JCH-205) has been deposited in the herbarium of the Botany Department, Postgraduate Jahan Zeb College, Saidu Sharif, Swat, Pakistan.

3.3 Extraction and isolation

The air-dried ground material (10 kg) was extracted with methanol at room temperature; the methanolic extract was evaporated to yield the residue (627 g) which was diluted in water and extracted with hexane, chloroform, ethyl acetate and finally with butanol. The butanolic extract (20 g) was chromatographed on silica gel column (70–230 mesh), eluting with $CHCl_3$, gradually increasing the solvent percentage of methanol to obtain 25 fractions. Fraction 22 (50.4 mg) was chromatographed by silica gel column chromatography ($CHCl_3$/MeOH, 25:75) and the semi-pure fraction obtained ($CHCl_3$/MeOH, 5:95) was purified by recycling HPLC to give compound **1** (30 mg). Fraction 10 (43.9 mg) was purified by silica gel column chromatography ($CHCl_3$/MeOH, 40:60) to give compound **2** (25 mg). Fraction 25 (60.5 mg) was purified by recycling HPLC preparation to give compounds **3** (25 mg) and **4** (20 mg).

3.3.1 Compound (*1*)

Light yellow oil; $[\alpha]_D^{25}$ −70 (*c* 0.0013, MeOH); UV λ_{max} (MeOH): 226, 207, 189 nm; IR(KBr) ν_{max} (cm^{-1}) 3507 (OH), 1770 (lactone). HRFAB–MS: *m/z* 543.1212 $[M + Na]^+$ (calcd for $C_{26}H_{32}O_{11}$ Na, 543.1880). ^1H NMR and ^{13}C NMR spectral data: see Table 1.

3.3.2 Compound (*2*)

Yellow oil; $[\alpha]_D^{25}$ −68.5 (*c* 0.0013, MeOH); UV λ_{max} (MeOH): 220, 208,195 nm; IR (KBr) ν_{max} (cm^{-1}) 3381–3015 (hydroxy), 1771 (lactone); HRFAB–MS: *m/z* 573.1317 $[M + Na]^+$ (calcd for $C_{27}H_{34}O_{12}$ Na, 573.1948). ^1H NMR and ^{13}C NMR spectral data: see Table 1.

3.3.3 Acid hydrolysis of compound *1*

Compound **1** (10 mg) was dissolved in 5 ml of 10% H_2SO_4/dioxane (1:1) and refluxed for 3.5 h at 100°C. The reaction mixture was diluted with water and extracted with $CHCl_3$. The aqueous layer was neutralised with $KHCO_3$ and sugar was identified by comparing with authentic samples of sugars on the TLC.

3.3.4 Acid hydrolysis of compound *2*

Compound **2** (10 mg) was hydrolysed with 2 M HCl in aqueous methanol (10 ml) at 100°C for 3 h. The methanol was evaporated under reduced pressure and the mixture was diluted with water and extracted with EtOAc. The EtOAc and water layers were evaporated under reduced pressure. The sugar was identified by comparing on the TLC with authentic samples of glucose using solvent system [EtOAc:MeOH:HOAc: H_2O (11:2:2:2)].

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