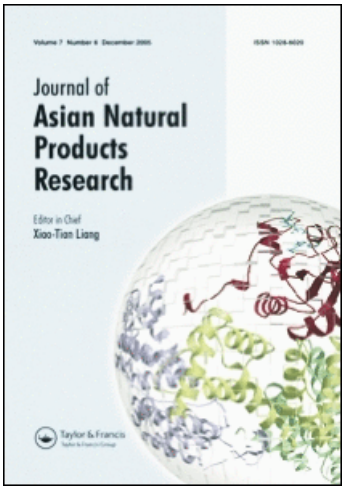

Journal of Asian Natural Products Research
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713454007

A new phenylpropanoid glycoside from *Leucas indica* Linn.

M. Mostafa[a]; Nasim Sultana[a]; Nilufar Nahar[b]; M. Mosihuzzaman[b]; M. Iqbal Choudhary[c]
[a] Chemical Research Division, BCSIR Laboratories, Dhaka, Bangladesh [b] Department of Chemistry, University of Dhaka, Dhaka, Bangladesh [c] H. E. J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi, Pakistan

To cite this Article Mostafa, M. , Sultana, Nasim , Nahar, Nilufar , Mosihuzzaman, M. and Choudhary, M. Iqbal(2009) 'A new phenylpropanoid glycoside from *Leucas indica* Linn.', Journal of Asian Natural Products Research, 11: 1, 29 — 32
To link to this Article: DOI: 10.1080/10286020802513848
URL: http://dx.doi.org/10.1080/10286020802513848

Journal of Asian Natural Products Research
Vol. 11, No. 1, January 2009, 29–32

Taylor & Francis
Taylor & Francis Group

A new phenylpropanoid glycoside from *Leucas indica* Linn.

M. Mostafa[a]*, Nasim Sultana[a], Nilufar Nahar[b], M. Mosihuzzaman[b] and M. Iqbal Choudhary[c]

[a]*Chemical Research Division, BCSIR Laboratories, Dhaka, Bangladesh;* [b]*Department of Chemistry, University of Dhaka, Dhaka, Bangladesh;* [c]*H. E. J. Research Institute of Chemistry, International Center for Chemical and Biological Sciences, University of Karachi, Karachi, Pakistan*

(*Received 4 April 2008; final version received 30 July 2008*)

A new phenylpropanoid glycoside, α-L-rhamnopyranosyl-(1 → 3)-*O*-α-L-rhamnopyranosyl-(1 → 6)-1-*O*-caffeoyl-β-D-glucopyranoside (**1**) along with two known phenylethanoid glycosides (**2**–**3**) has been isolated from the aerial parts of *Leucas indica* Linn. Their structures were deduced from the spectroscopic studies and compared with the literature values.

Keywords: *Leucas indica* L.; caffeoyl-β-D-glucopyranoside; phenylpropanoid glycosides

1. Introduction

Leucas indica Linn. (Syn: *L. lavandulaefolia* Sm, local name: Dandakalos, family: Labiatae) is used as a folk medicine in Bangladesh for the treatment of headaches, cough, cold, scabies, and vermifuge [1]. Antibacterial, wound healing, antidiarrheal, antitussive and hypoglycemic activities of this plant have been reported earlier [2–6]. There are few reports on its chemical investigations [7,8]. We have previously described the isolation of six phenylethanoid glycosides with antioxidant activities from the same plant [9]. In continuation of this work, a new phenylpropanoid glycoside, α-L-rhamnopyranosyl-(1 → 3)-*O*-α-L-rhamnopyranosyl-(1 → 6)-1-*O*-caffeoyl-β-D-glucopyranoside (**1**) was isolated along with two known phenylethanoid glycosides, β-(3-hydroxy-4-methoxy-phenyl)-ethyl-*O*-(β-D-glucopyranosyl)-(1 → 2)-*O*-(α-L-rhamnosyl)-(1 → 3)-6-*O*-*E*-feruloyl-β-D-glucoside (**2**) (incanoside A) [10] and β-(3,4-dihydroxy-phenyl)-ethyl-*O*-(α-L-rhamnosyl)-(1 → 3)-*O*-(β-D-glucoside)-(1 → 6)-4-*O*-*E*-caffeoyl-β-D-glucoside (**3**) [11].

2. Results and discussion

Compound **1** was isolated as a brown amorphous powder by HPLC from the *n*-butanol soluble part. The molecular formula was deduced as $C_{27}H_{38}O_{17}$ from its negative ion of FABMS (*m/z* 633, $[M - H]^-$) and ^{13}C NMR spectral data. The molecular formula was also confirmed by HR-FAB-MS at *m/z* 633.2048 $[M - H]^-$. The UV spectrum displayed absorption maxima at 330, 263, and 203 nm indicating its phenolic nature. The IR spectrum showed the presence of hydroxyl (3419 cm^{-1}), α,β-unsaturated ester (1700, 1631 cm^{-1}), and the aromatic >C=C< (1601, 1515 cm^{-1}) functionalities. The ^1H NMR, ^1H–^1H COSY, ^{13}C NMR, HMQC and HMBC spectra displayed characteristic signals for the caffeoyl, glucose, and rhamnose moieties. The ^1H NMR spectrum exhibited three aromatic proton signals at δ_H 7.04 (brs, H-2), 6.76 (d, $J = 8.0$ Hz, H-5), and 6.94 (brd, $J = 8.0$ Hz, H-6) and two olefinic protons at δ_H 7.58 (d, $J = 15.8$ Hz, H-7) and 6.26 (d, $J = 15.8$ Hz, H-8) indicating a *trans* caffeoyl moiety. Three signals for anomeric protons

*Corresponding author. Email: mostafabcsir@yahoo.com

ISSN 1028-6020 print/ISSN 1477-2213 online

DOI: 10.1080/10286020802513848
http://www.informaworld.com

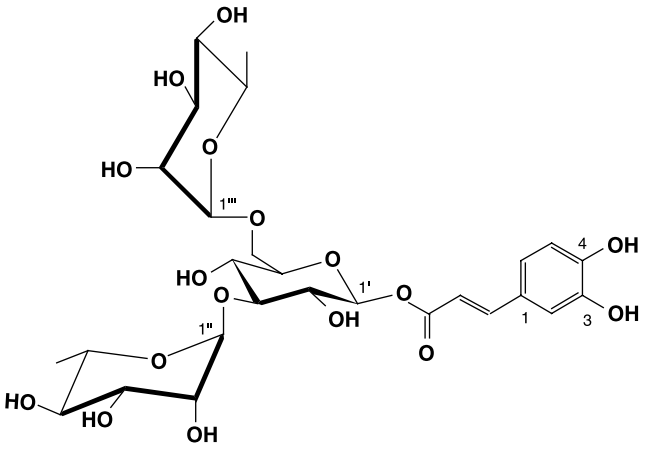

Figure 1. The structure of compound **1**.

at δ_H 4.36 (d, $J = 7.8$ Hz, H-1′), 5.17 (brs, H-1″), and 4.61 (brs, H-1‴) and for the terminal methyl groups at δ 1.18 (d, $J = 6.0$ Hz) and 1.07 (d, $J = 6.0$ Hz) indicated that compound **1** possessed one β-linked glucose and two α-linked rhamnose residues. The ^{1}H and ^{13}C NMR spectral data of compound **1** were compared with the reported phenylpropanoid [12] and deduced to have an additional α-L-rhamnose moiety.

Linkage of the caffeoyl moiety to C-1′ of glucose was deduced by the cross peak in the HMBC spectrum, between H-1′ (δ 4.36) and the carbonyl carbon (δ 169.5). The HMBC correlations between H-1″ (δ_H 5.17, bs) of rhamnose with C-3′ (δ_c 81.6) of glucose and H-1‴ (δ 4.61, bs) of rhamnose with C-6′ (δ_c 67.6) of glucose indicated that the former rhamnose residue was located at the C-3′ and the latter one at the C-6′ position of central glucose moiety. The structure of compound **1** was thus established as (α-L-rhamnopyranosyl)-(1 → 3′)-*O*-(α-L-rhamnopyranosyl)-(1 → 6′)-1-*O*-*E*-caffeoyl-β-D-glucopyranoside (Figure 1).

The known compounds **2**–**3** were identified by the comparison of their physical and spectral data with those of literature values as β-(3-hydroxy-4-methoxy-phenyl)-ethyl-*O*-(β-D-glucopyranosyl)-(1 → 2)-*O*-(α-L-rhamnosyl)-(1 → 3)-6-*O*-*E*-feruloyl-β-D-glucoside (**2**) (incanoside A), and β-(3,4-dihydroxy-phenyl)-ethyl-*O*-(α-L-rhamnosyl)-(1 → 3)-*O*-(β-D-glucoside)-(1 → 6)-4-*O*-*E*-caffeoyl-β-D-glucoside (**3**). These compounds were previously reported from other natural sources [10,11] and this is the first report of them isolated from *L. indica*.

3. Experimental

3.1 General experimental procedures

Optical rotations were measured on JASCO DIP-360 digital polarimeter. UV spectra were measured in MeOH on a Shimadzu UV 240 spectrophotometer. IR spectra were recorded in KBr on a JASCO A-302 spectrophotometer. ^{1}H- (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AMX-400 spectrometer with tetramethylsilane (TMS) as an internal standard. The 2D NMR spectra were recorded on a Bruker AMX 500 NMR spectrometer. Fast atom bombardments mass measurements (FAB-MS) were conducted in glycerol matrixes on JEOL HX110 mass spectrometer. TLC was carried out on a pre-coated silica gel on aluminum sheets (E-Merck, Darmstadt, Germany). For column chromatography, silica gel (E-Merck, 230–400 mesh) was used. HPLC was performed out using Shim pack PRC-ODS column (solvent: MeOH in H_2O) with UV detector.

3.2 Plant material

The aerial parts of *L. indica* Linn. were collected from the Shaistagonj, Hobigong district, Bangladesh, which was identified by Prof. Salar Khan. A voucher specimen of the plant (voucher No. 29354) was deposited at the Bangladesh National Herbarium (BNH), Dhaka, Bangladesh.

3.3 Extraction and isolation

The aerial parts of the plant were cleaned, cut into small pieces, and dried in an oven below 40°C. The dried materials were ground to powder (7.1 kg) and successively extracted with CH_2Cl_2 (18 l × thrice, 24 h, at room temperature) and MeOH (16 l × thrice, 24 h, at room temperature). The extracts were then filtered and dried below 40°C under vacuum and finally freeze dried to get CH_2Cl_2 (190 g) and MeOH extracts (536.3 g). The methanol extract (536 g) was suspended in H_2O and partitioned with 10% methanol in ethyl acetate. The aqueous part of MeOH extract (after partition with 10% MeOH in EtOAc) was partitioned with *n*-BuOH. The *n*-BuOH soluble part (70 g) was chromatographed over silica gel column using EtOAc–BuOH–MeOH–H_2O (65:20:0.5:0.5) as solvent and 10 fractions were obtained (LIB1–LIB10). The fraction LIB2 (550 mg) was further chromatographed over RP-18 silica gel column using the solvent system MeOH: H_2O (35:65), which yielded compound **3** (30 mg). The fraction LIB3 (12.5 g) was further chromatographed by RP-18 silica gel column using MeOH–H_2O in order of increasing polarity (from 10% methanol in water to 100% methanol), which yielded six subfractions (LIB3-1–LIB3-6). The subfraction LIB3-2 (1.27 g) was again chromatographed by HPLC using 40% MeOH in H_2O which yielded six fractions (LIB3-2-1–LIB3-2-6). The fraction LIB3-2-1 was further fractionated by HPLC (Shim pack PRC-ODS column, flow rate 1 ml/min, UV detector 254 nm) using 38% MeOH in H_2O which afforded compound **1** (8 mg). The subfraction LIB3-2-4 (55.5 mg) was further subjected to purification by HPLC (Shim pack PRC-ODS column, flow rate 1 ml/min, UV detector 254 nm) using 60% MeOH in H_2O which yielded compound **2** (10 mg).

3.3.1 *α-L-Rhamnopyranosyl-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 6)-1-O-caffeoyl-β-D-glucopyranoside (**1**)*

Brown amorphous powder; $[\alpha]_D^{22}$-55.6 (MeOH, C 0.25); UV (MeOH) λ_{max}: 330, 327, 263, 203, 194 nm; IR ν_{max} (KBr): 3419, 1700, 1631, 1601, 1515, 1393, 1272, and 1032 cm^{-1}; ^1H NMR (400 MHz, CD_3OD) and ^{13}C NMR spectral data are shown in Table 1; FAB-MS (negative mode) *m/z* 633 $[M - H]^-$; HR-FAB-MS (negative mode) *m/z* 633.2048 $[M - H]^-$ (calcd for $C_{27}H_{37}O_{17}$, 633.2030).

Table 1. ^1H and ^{13}C NMR spectral data of compound **1** (400 MHz for ^1H and 100 MHz for ^{13}C, respectively, in CD_3OD, δ ppm).

No.	δ_H (mult., *J* in Hz)	No.	δ_C
1	–	1	127.7
2	7.04 (brs)	2	115.3
3	–	3	147.4
4	–	4	149.7
5	6.76 (d, 8.0)	5	116.6
6	6.94 (brd, 8.0)	6	123.2
7	7.58 (d, 15.8)	7	148.0
8	6.26 (d, 15.8)	8	114.8
9	–	9	169.5
1′	4.36 (d, 7.8)	1′	104.4
2′–3′	3.25–3.98 (m[a])	2′	76.2
4′	4.96 (t, 9.5)	3′	81.6
5′	3.25–3.98 (m[a])	4′	70.4
6′	3.45 (m), 3.72 (m)	5′	74.8
1″	5.17 (brs)	6′	67.6
2″–5″	3.25–3.98 (m[a])	1″	103.0
6″	1.18 (d, 4.4)	2″	72.4
1‴	4.61 (brs)	3″	72.1
2‴–5‴	3.25–3.98 (m[a])	4″	74.0
6‴	1.07 (d, 6.0)	5″	69.9
		6″	18.4
		1‴	102.3
		2‴	72.1
		3‴	72.4
		4‴	73.9
		5‴	70.4
		6‴	18.0

[a]May be interchanged in each column.

Acknowledgements

The authors are grateful to Asian Network of Research on Antidiabetic Plants (ANRAP) and Human Resource Development Project, Bangladesh Council of Scientific and Industrial Research (BCSIR) for financial support to one of the authors (M.M.). A major part of this work was carried out at the H.E.J. Research Institute of Chemistry.

References

[1] M. Yusuf, J.U. Chowdhury, M.A. Waheb, and J. Begum, *Medicinal Plants of Bangladesh* (BCSIR, Dhaka, Bangladesh, 1994), pp. 149–151.

[2] K. Saha, P.K. Mukherjee, S.C. Mandal, M. Pal, and B.P. Saha, *Indian Drugs* **32**, 402 (1995).

[3] K. Saha, P.K. Mukherjee, J. Das, M. Pal, and B.P. Saha, *J. Ethnopharmacol*. **56**, 139 (1997).

[4] P.K. Mukherjee, K. Saha, T. Murugesan, S.C. Mandal, M. Pal, and B.P. Saha, *J. Ethnopharmacol*. **60**, 85 (1998).

[5] K. Saha, P.K. Mukherjee, T. Murugesan, B.P. Saha, and M. Pal, *J. Ethnopharmacol*. **57**, 89 (1997).

[6] K. Saha, P.K. Mukherjee, J. Das, S.C. Mandal, M. Pal, and B.P. Saha, *Phytother. Res.* **11**, 463 (1997).

[7] J.E. Smith and P.A. Victor, *Acta Pharm.* **10**, 27 (1985).

[8] S.B. Mahato and B.C. Pal, *Phytochemistry* **25**, 909 (1986).

[9] M. Mostafa, N. Nahar, M. Mosihuzzaman, T. Makhmoor, M.I. Choudhary, and A.-U. Rahman, *Nat. Prod. Res.* **21**, 354 (2007).

[10] J.J. Gao, G.Q. Han, and L. Yang, *Chin. Chem. Lett.* **7**, 445 (1996).

[11] C. Andary, H. Ravn, R. Wylde, A. Heitz, and E. Motte-Florac, *Phytochemistry* **28**, 288 (1989).

[12] J.C. Ho, C.M. Chen, Z.Q. Li, and L.C. Row, *J. Chin. Chem. Soc.* **51**, 1073 (2004).