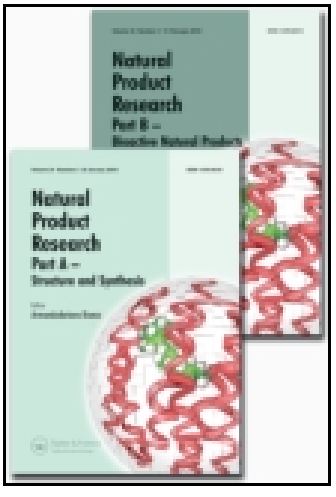

Natural Product Research: Formerly Natural Product Letters
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gnpl20

Gallic acid esters from the stem bark of Mimusops elengi L.

Nida Akhtar [a] , Mohd. Ali [b] & Mohd. Sarwar Alam [a]

[a] Department of Chemistry, Faculty of Science , Jamia Hamdard (Hamdard University) , New Delhi-110 062, India

[b] Department of Pharmacognosy and Phytochemistry, Faculty of Pharmacy , Jamia Hamdard (Hamdard University) , New Delhi-110 062, India

Published online: 19 May 2010.

To cite this article: Nida Akhtar , Mohd. Ali & Mohd. Sarwar Alam (2010) Gallic acid esters from the stem bark of Mimusops elengi L., Natural Product Research: Formerly Natural Product Letters, 24:10, 962-972, DOI: 10.1080/14786410902833989

To link to this article: http://dx.doi.org/10.1080/14786410902833989

Natural Product Research
Vol. 24, No. 10, 15 June 2010, 962–972

Gallic acid esters from the stem bark of *Mimusops elengi* L.

Nida Akhtar[a], Mohd. Ali[b]* and Mohd. Sarwar Alam[a]

[a]*Department of Chemistry, Faculty of Science, Jamia Hamdard (Hamdard University), New Delhi – 110 062, India;* [b]*Department of Pharmacognosy and Phytochemistry, Faculty of Pharmacy, Jamia Hamdard (Hamdard University), New Delhi – 110 062, India*

(*Received 17 December 2008; final version received 20 March 2009*)

Phytochemical investigation of the ethanolic extract of the stem bark of *Mimusops elengi* L. (Sapotaceae) led to the isolation of new gallic acid esters, characterised as phenyl propanoxyl gallate (**1**), β-D-glucopyranosyl (6′→1″)–β-D-glucopyranosyl-4″-(4″-ethylphenyl) gallate (**2**), 2′-(1‴-geranyloxy)-β-D-glucopyranosyl (6′→1″)-β-D-glucopyranosyl-4″-phenoxy gallate (**3**), β-D-glucopyranosyl (6′→1″)–β-D-glucopyranosyl 3,4,5-trihydroxy benzoate (**4**), β-D-glucopyranosyl-(6'→1″)–β-D-glucopyranosyl-4″-(4‴-*n*-butylphenyl) 3,4,5-trihydroxy benzoate (**5**), β-D-glucopyranosyl(6'→1″)-β-D-rhamnosyl 3,4,5-trihydroxy benzoate (**6**) and β-D-(2′-phenyl glucopyranosyl)-(6′→1″)–(2″,4″-diphenylrhamnopyranosyl)-3,4,5-trihydroxylbenzoate (**7**), along with the known compounds: farnon-3-one, stigmasta-5-en-3-β-ol, olean-18-en-2-one-3-ol, lup-20(29)-en-3β-ol and stigmasta-5-en-3β-D-glucopyranoside. Their structures were elucidated on the basis of spectroscopic analyses and chemical reactions.

Keywords: *Mimusops elengi* L.; Sapotaceae; stem bark; ethanolic extract; gallic acid esters

1. Introduction

Mimusops elengi L. (Sapotaceae) is a large glabrous evergreen tree found in the western Peninsula of India (Anonymous, 2003). The tree is planted throughout India for its ornamental foliage and the fragrance of its flowers (Kirtikar & Basu, 1993). Its bark is acrid, sweet, cardiotonic, alexipharmic, stomachic, anthelmintic, astringent, and is also used to cure biliousness and diseases of the gums and teeth (Drury, 1873; Kirtikar & Basu, 1993). It has exhibited antimicrobial, anti-ulcer, hypotensive, anti-HIV and spasmolytic activities (Banerji, Prakash, Patnaik, & Nigam, 1982; Dar, Behbahanian, Malik, & Jahan, 1999; Mundhada & Takte, 2005; Sahu, Mandal, Banerjee, & Siddiqui, 2001; Shah, Gandhi, Shah, Goswami, & Santani, 2003). Ursolic acid, betulinic acid, the fatty acid ester of α-spinasterol (Misra, Nigam, & Mitra, 1974), 3β,6β,19β,23-tetrahydroxy-urs-12-ene, 1β-hydroxy-3β-hexanoyllup-20(29)-ene-23,28-dioic acid and basic acid have been isolated from its bark (Jahan et al., 2001; Varshney & Logani, 1969).

*Corresponding author. Email: mali_hamdard@yahoo.co.in; maliphyto@gmail.com

ISSN 1478–6419 print/ISSN 1029–2349 online

DOI: 10.1080/14786410902833989
http://www.informaworld.com

2. Results and discussion

Compound **1**, designated as elengigallate, was obtained as a pale brown amorphous powder from chloroform:methanol (93:7) eluants. It gave a blue colour with aqueous ferric chloride solution, indicating the phenolic nature of the molecule. Its IR spectrum exhibited distinctive absorption bands for hydroxyl groups (3391, 3110 cm^{-1}), an ester group (1723 cm^{-1}) and unsaturation (1608 cm^{-1}). It had a molecular ion peak at m/z 288 in its mass spectrum, corresponding to a molecular formula of $C_{16}H_{16}O_5$, for an alkylated diphenyl-type molecule. The ^{1}H NMR spectrum of **1** displayed two one-proton doublets at δ 7.28 ($J = 2.5$ Hz) and 7.26 ($J = 2.5$ Hz) assigned to meta-coupled H-2 and H-6 aromatic protons. Two multiplets at δ 6.93 and 6.90 integrating for two protons each and a one-proton multiplet at δ 6.88 were attributed to aromatic protons of the second ring. A two-proton broad multiplet at δ 3.55 was associated with the oxygenated methylene proton H_2-9′. Two two-proton multiplets at δ 2.74 and 1.52 were ascribed to H_2-7′ and H_2-8′, methylene protons. The ^{13}C NMR spectrum of **1** showed important signals for an ester carbon at 167.49 (C-7), aromatic carbons between δ 158.74 and 107.10, oxygenated methylene carbons at δ 60.76 (C-9′) and methylene carbons at δ 29.04 (C-7′), 28.71 (C-8′). The DEPT spectrum of **1** exhibited the presence of three methylene, seven methine and six quaternary carbons. The HMBC spectrum of **1** showed correlations of C-7 with H-2/H-6 and H_2-9′, and C-1′ with H_2-7′ and C-2′/6′. Acid hydrolysis of **1** yielded gallic acid (TLC comparable). On the basis of this spectral data analysis and chemical reactions, the structure of **1** has been elucidated as phenyl propanoxyl gallate.

Compound **2**, named mimusopstannin, was obtained as a brown-coloured amorphous mass from chloroform:methanol (93:7) eluants. It responded positively to a test for phenols and glycosides. Its IR spectrum exhibited distinctive absorption bands for hydroxyl groups (3369, 3290 and 3160 cm^{-1}), an ester group (1722 cm^{-1}) and unsaturation (1606 cm^{-1}). On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 598, consistent with the molecular formula of a gallic acid diglucoside substituted with a phenoxy group, $C_{27}H_{34}O_{15}$. The ^{1}H NMR spectrum of **2** showed a two-proton doublet at δ 7.51 ($J = 2.6$ Hz) assigned to meta-coupled H-2 and H-6 protons. Two multiplets at δ 7.45 and 5.23, integrating for two protons each, were ascribed to aromatic H-2‴, H-6‴and H-3‴, H-5‴ protons, respectively. Two doublets at δ 5.23 ($J = 7.2$ Hz) and 5.01 ($J = 7.1$ Hz) were attributed to anomeric H-1′ and H-1″ protons, respectively. The remaining sugar protons appeared between at δ 4.56 and 3.38. The deshielded signals at δ 4.03 (H-4″) and 3.46 (H_2-6′) supported the location of the phenoxy ring at C-4″ and another sugar linkage at C-6′. A two-proton multiplet at δ 2.73 and a three-proton triplet at δ 0.82 ($J = 7.8$ Hz) were accounted to methylene H_2-7‴ protons attached to the phenyl ring and primary methyl H_3-8‴ protons, respectively. The ^{13}C NMR spectrum of **2** exhibited signals for an ester carbon in deshielded range at δ 169.13 (C-7), aromatic carbons between δ 159.06 and 110.16, a C-7‴ methylene carbon at δ 18.12, a methyl carbon at δ 8.9, anomeric carbons at δ 102.97 (C-1′) and 100.09 (C-1″), and sugar carbons between δ 75.50 and 60.88. The C-6′ at δ 65.84 and C-4″ at δ 69.88 were shifted in a deshielded region due to the attachment of the second sugar moiety and phenoxy group, respectively. The DEPT spectrum of **2** showed the presence of one methyl, three methylene, 16 methine and seven quarternary carbons. The HMBC

spectrum of **2** displayed the interaction of C-7 with H-2/6 and H-1′, C-1″ with H_2-6′ and H-2″, and C-1‴ with H-4″ and H-2‴/6‴. Acid hydrolysis of **2** yielded gallic acid and glucose (TLC comparable). On the basis of the above findings, the structure of **2** has been elucidated as β-D-glucopyranosyl (6'→1″)–β-D-glucopyranosyl-4″-(4‴-ethylphenyl) gallate.

Compound **3**, designated as elengitannin, was obtained as a yellowish brown amorphous mass from chloroform:methanol (93:7) eluants. It gave a positive test for phenols and glycosides. Its IR spectrum exhibited absorption bands for hydroxyl groups (3435, 3260 cm^{-1}), an ester group (1722 cm^{-1}) and unsaturation (1610 cm^{-1}). On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 698, consistent with a molecular formula $C_{34}H_{50}O_{15}$, corresponding to a gallic acid diglycoside attached to monoterpenic and phenyl moieties. The mass spectrum showed prominent ion fragments at m/z 239 $[C_6H_{10}O_5–C_6H_5]^+$, 255 $[C_6H_{10}O_6–C_6H_5]^+$, 459 $[M–239]^+$ and 443 $[M–255]^+$, indicating the location of the phenyl ring to the terminal sugar moiety. The ion fragments arising at m/z 153 $[CO–C_6H_3(OH)_3]^+$, 169 $[OCO–C_6H_3(OH)_3]^+$ and 313 $[C_6H_{10}O_5–CO\ C_6H_3(OH)_3]^+$ supported the attachment of gallic acid with a glucose moiety. The ion peaks generated at m/z 141 $[C_{10}H_{21}]^+$ and 157 $[C_{10}H_{21}O]^+$ suggested that an acyclic monoterpenic moiety was linked to the sugar residue. The ^1H NMR spectrum of **3** showed a 2-proton doublet at δ 7.45 ($J = 2.3$ Hz) assigned to meta-coupled H-2 and H-6 protons, and three multiplets at δ 7.43 (2H), 7.40 (2H) and 6.92 (1H) ascribed to the remaining aromatic protons. Two one-proton doublets at δ 5.26 ($J = 7.1$ Hz) and 4.96 ($J = 6.9$ Hz) were attributed to anomeric H-1′ and H-1″ protons, respectively. The remaining sugar protons resonated between δ 4.03 and 3.19. The shifting of the ^1H NMR signal at δ 3.62 (H-4″), 3.43 (H_2-6′) in the deshielded region indicated the attachment of a phenoxy group at C-4″ and another sugar–sugar moiety at C-6′. The oxygenated methylene protons appeared as broad signals at δ 3.43 (H_2-6), 3.21 (H_2-1″) and 3.19 (H_2-1‴). A three-proton doublet at δ 1.03 ($J = 6.1$ Hz) and a six-proton broad signal at δ 0.79 were associated with the secondary C-8‴ methyl and two C-9‴ and C-10‴ methyl protons, respectively. The other methine and methylene protons resonated between δ 2.51 and 1.18. The ^{13}C NMR spectrum of **3** displayed signals for an ester carbon at δ 167.49 (C-7), aromatic carbons between 158.68 and 110.27, anomeric carbons at δ 107.14 (C-1′) and 102.94 (C-1″), sugar carbons between δ 76.81 and 61.93, and monoterpenic carbons in the range δ 60.90–11.51. The HMBC spectrum of **3** showed correlation of C-7 with H-1′ and H-2/6, C-1″ with H-2″ and H_2-6′, and C-1a with H-4″ and C-1‴ with H-2′ and H_2-2‴. Acid hydrolysis of **3** yielded gallic acid (TLC comparable). On the basis of the above-mentioned findings, the structure of **3** has been elucidated as 2′-(1‴-geranyloxy)-β-D-glucopyranosyl (6′→1″)-β-D-glucopyranosyl-4″-phenoxy gallate.

Compound **4**, designated as gallic acid diglucoside, was obtained as colourless amorphous powder from chloroform:methanol (23:2) eluants. Its IR spectrum exhibited absorption bands for hydroxyl groups (3366, 3210 and 3060 cm^{-1}) and an ester group (1723 cm^{-1}). It had a molecular ion peak at m/z 494 in its mass spectrum, corresponding to a molecular formula of gallic acid diglycoside, $C_{19}H_{26}O_{15}$. The ^1H NMR spectrum of **4** displayed two one-proton doublets at δ 7.52 ($J = 3.0$ Hz) and 7.44 ($J = 3.0$ Hz) assigned to meta-coupled aromatic H-2 and H-6 protons, respectively. Two one-proton doublets at δ 4.99 ($J = 6.6$ Hz) and 4.96 ($J = 6.6$ Hz) were ascribed to anomeric protons H-1′ and H-1″, respectively. Two broad signals at δ 3.38

and 3.28, both integrating for two-protons each, were attributed as corresponding to oxygenated methylene protons H_2-6′ and H_2-6″, and a deshielded signal at δ 3.38 indicated that the second sugar proton was attached to the H_2-6′ group. The remaining carbinol protons of the sugar units appeared between δ 4.04 and 3.40. The ^{13}C NMR spectrum of **4** showed an important signal for an ester carbon at δ 170.12 (C-7), aromatic carbons in the range of δ 162.98–111.36, anomeric carbons at δ 110.22 (C-1′) and 102.89 (C-1″) and sugar carbons between δ 75.50 and 60.90. The presence of C-6′ resonance in the deshielded region at δ 65.84 supported attachment of the second sugar moiety at C-6′. The HMBC spectrum of **4** showed interactions of C-7 with H-1′ and H-2/6, and C-1″ with H_2-6′ and H-2″. Acid hydrolysis of **4** yielded gallic acid and D-glucose (TLC comparable). On the basis of this spectral data analysis and chemical reactions, the structure of **4** has been established as β-D-glucopyranosyl (6′→1″)–β-D-glucopyranosyl 3,4,5-trihydroxy benzoate.

Compound **5**, designated as gallic acid phenoxy diglucoside, was obtained as a pale brown coloured amorphous powder from chloroform:methanol (23:2) eluants. It gave a positive test for phenols and glycosides. Its IR spectrum exhibited characteristic absorption bands for hydroxyl groups (3362, 3310 and 3260 cm^{-1}) and an ester group (1722 cm^{-1}). On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 626, consistent with the molecular formula $C_{29}H_{38}O_{15}$ for a gallic acid diglucoside substituted with a phenyl ring. The ^{1}H NMR spectrum of **5** showed two one-proton doublets at δ 7.51 ($J = 2.7$ Hz) and 7.44 ($J = 2.7$ Hz) assigned to meta-coupled aromatic H-2 and H-6 protons, respectively. Two multiplets at δ 6.92 and 6.88, integrated for two-protons each, were ascribed the aromatic H-2‴, H-6‴ and H-3‴, H-5‴ protons, respectively. Two one-proton doublets at δ 5.48 ($J = 7.0$ Hz) and 4.94 ($J = 7.2$ Hz) were attributed correspondingly to anomeric H-1′ and H-1″. The remaining sugar protons appeared in the range of δ 4.53–3.28. The shifting of oxygenated methylene H_2-6′ protons at δ 3.40 and 3.36, and the carbinol H-4″ proton at δ 4.04 in the deshielded region indicated the attachment of the second sugar moiety at C-6′ and a phenyl group at C-4″. Three two-proton signals as a multiplet at δ 2.51 and as broad signals at δ 0.92 and 0.87 were associated with the methylene H_2-7‴, H_2-8‴ and H-9″ protons. A three-proton triplet at δ 0.62 ($J = 6.5$ Hz) was accounted to primary C-10‴ methyl protons. The ^{13}C NMR spectrum of **5** displayed signals for an ester carbon at δ 171.66 (C-7), aromatic carbons between δ 167.43 and 108.71, anomeric carbons at δ 100.10 (C-1′) and 103.12 (C-1″), other sugar carbons in the range of δ 76.90–61.07, methylene carbons at δ 33.16 (C-7‴), 29.15 (C-8‴) and 28.98 (C-9‴), and methyl carbons at δ 17.09 (C-10‴). The DEPT spectrum of **5** showed the presence of one methyl, five methylene, 16 methine and seven quaternary carbons. The HMBC spectrum of **5** exhibited correlation of C-7 with H-2/6 and H-1′, C-1″ with H_2-6′ and H-2″, C-1‴ with H-4″ and H-2‴/6‴, and C-10‴ with H_2-9‴. Acid hydrolysis of **5** yielded gallic acid and glucose. On the basis of the above-mentioned data, the structure of **5** has been elucidated as β-D-glucopyranosyl-(6′→1″)–β-D-glucopyranosyl-4″-(4‴-*n*-butylphenyl)3,4,5-trihydroxy benzoate.

Compound **6**, designated as elengibenzyl diglycoside, was obtained as a brown coloured amorphous mass from chloroform:methanol (9:1) eluants. It gave a positive test for phenols and glycosides. Its IR spectrum exhibited characteristic absorption bands for hydroxyl groups (3384 and 3280 cm^{-1}) and an ester group (1722 cm^{-1}).

On the basis of mass and ^{13}C NMR spectra, its molecular weight was established as 478, consistent with the molecular formula of a gallic acid diglycoside, $C_{19}H_{26}O_{14}$. The ^{1}H NMR spectrum of **6** showed two one-proton deshielded doublets at δ 7.58 ($J = 2.5$ Hz) and 7.51 ($J = 2.5$ Hz) assigned to meta-coupled H-2 and H-6, respectively. Two one-proton doublets at δ 5.54 ($J = 7.1$ Hz) and 5.01 ($J = 7.2$ Hz) were ascribed correspondingly to anomeric H-1′ and H-1″ protons. The remaining sugar protons appeared in the range of δ 4.09–3.38. A three-proton doublet at δ 1.20 ($J = 6.2$ Hz) was accounted to the C-6″ methyl proton of rhamnose unit. The shifting of the C-6′ oxygenated methylene protons in the deshielded region at δ 3.38 indicated the attachment of a second monosaccharide unit at C-6′. The ^{13}C NMR spectrum of **6** displayed signals for an ester carbon at 169.11 (C-7), anomeric signals at δ 102.97 (C-1′) and 100.12 (C-1″), other sugar carbons in the range δ 75.54–63.08, a methyl carbon at δ 17.88 (C-6″) and aromatic carbons between δ 158.65 and 110.19. The HMBC spectrum of **6** showed the correlations C-7 with H-1′ and H-2/H-6, C-1″ with H_2-6′ and H-2″, and C-6″ with H-5″. Acid hydrolysis of **6** yielded gallic acid, glucose and rhamnose (TLC comparable). On the basis of the above-mentioned discussion, the structure of **6** has been elucidated as β-D-glucopyranosyl (6′→1″)-β-D-rhamnosyl 3,4,5-trihydroxy benzoate.

Compound **7**, designated as gallic acid triphenoxy diglycoside, was obtained as a light brown amorphous powder from chloroform:methanol (9:1) eluants. It responded positively to the test for phenols and glycosides. Its IR spectrum exhibited characteristic absorption bands for hydroxyl groups (3480, 3396 and 3285 cm^{-1}), an ester group (1723 cm^{-1}) and unsaturation (1607 cm^{-1}). On the basis of mass and ^{13}C NMR spectra its molecular weight was established as 706, consistent with the molecular formula $C_{37}H_{38}O_{14}$ of a gallic acid diglucoside substituted with phenyl rings. The prominent ion fragments generated at m/z 391, 315 [C_4′–O fission]$^+$ suggested that rhamnose was the terminal sugar to which two phenyl rings were attached. The ion peaks arising at m/z 153 [C_7–O fission]$^+$ and 125 [C_1–C_7 fission]$^+$ indicated the location of the gallic acid moiety attached to the glucose. The ^{1}H NMR spectrum of **7** showed two one-proton doublets at δ 7.98 ($J = 2.3$ Hz) and 7.69 ($J = 2.3$ Hz) assigned to meta-coupled aromatic H-2 and H-6 protons, respectively. Seven multiplets between δ 7.86 and 6.73 were ascribed to the other aromatic protons. Two one-proton doublets at δ 5.17 ($J = 7.1$ Hz) and 5.12 ($J = 7.0$ Hz) were attributed to anomeric H-1′ and H-1″ protons, respectively. A three-proton doublet at δ 1.30 ($J = 6.5$ Hz) was accounted to the C-6″ secondary methyl proton of the rhamnose unit. The remaining sugar protons resonated in the range δ 4.29–3.35. The deshielded two-proton oxygenated methylene proton signal at δ 3.35 indicated the attachment of the second sugar unit at C-6′. The ^{13}C NMR spectrum of **7** showed signals for an ester carbon at δ 169.13 (C-7), aromatic carbons in the range δ 158.49–110.24, anomeric carbons at δ 103.01 (C-1′) and 100.13 (C-1″), sugar carbons between δ 75.48 and 60.91, and a methyl carbon at δ 17.94 (C-6″). The HMBC spectrum of **7** exhibited that C-7 interacted with H-1′ and H2/6, C-1″ interacted with H-2″ and H_2-6′ and aromatic C-1 interacted with aromatic H-2/H-6, H-2′/2″ and H-4″. Acid hydrolysis of **7** yielded gallic acid, glucose and rhamnose (TLC comparable). On the basis of the above-mentioned findings, the structure of **7** has been elucidated as β-D-(2′-phenylglucopyranosyl)-(6′→1″)–(2″,4″-diphenylrhamnopyranosyl)-3,4,5-trihydroxybenzoate (Figure 1).

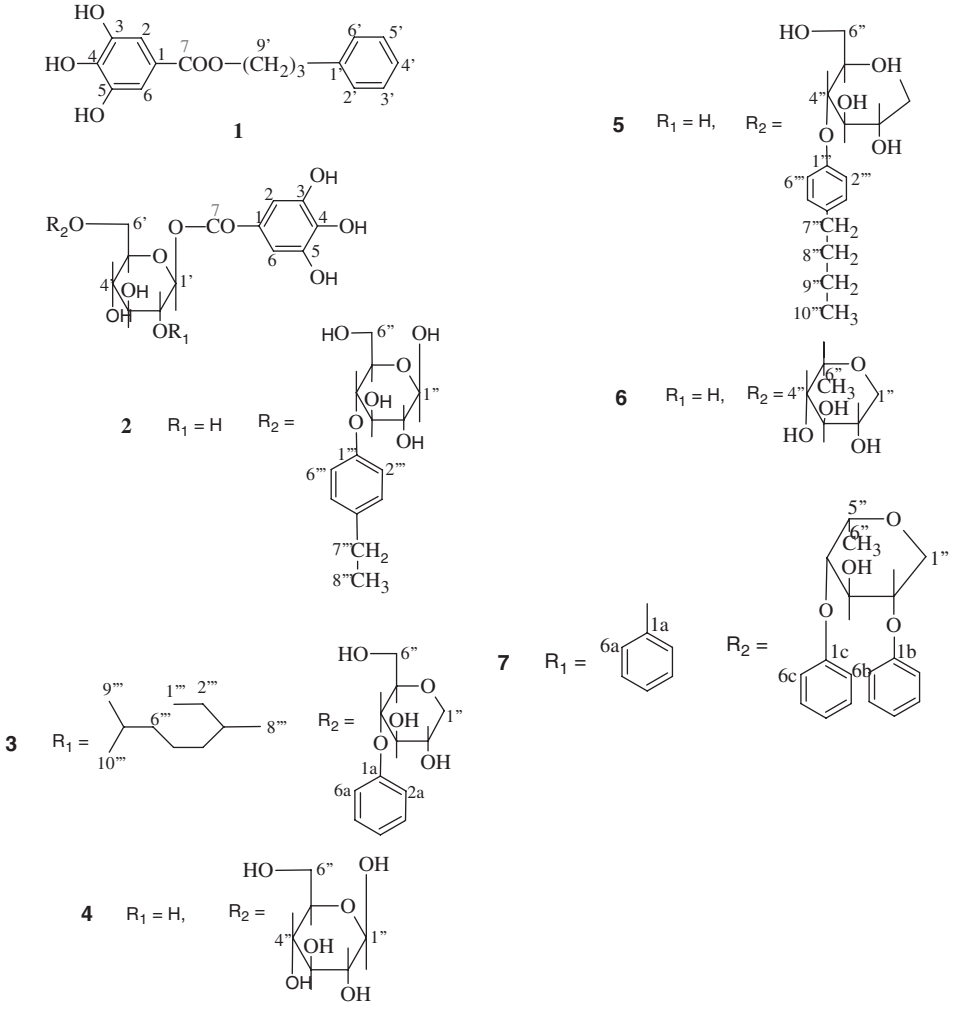

Figure 1. Structures of compounds **1**–**7**.

3. Experimental

3.1. *General experimental procedures*

Melting points were determined on a Perfit melting point apparatus (Ambala, India) and are uncorrected. IR spectra were recorded on KBr discs, using a Bio-Rad FT-IR 5000 spectrometer (FTS 135, Hongkong). UV spectra were measured with a Lambda Bio 20 spectrophotometer (Perkin Elmer, Switzerland) in methanol. ^{1}H and ^{13}C NMR spectra were scanned using Bruker Advance DRY 400 spectrospin and Bruker Advance DRY 100 spectrospin instruments (Germany), respectively, in $CDCl_3$ and with TMS as an internal standard. FAB MS spectra were obtained using a Jeol-JMS-DX 303 spectrometer (USA). Column chromatography was performed on silica gel (Qualigens, Mumbai, India) 60–120 mesh. TLC was run on silica gel G (Qualigens, Mumbai, India). Spots were visualised when exposed to iodine vapours, UV radiation and by spraying reagents.

3.2. *Plant material*

The barks of *M. elengi* were purchased from the Khari Baoli local market of Delhi and authenticated by Dr H.B. Singh, Taxonomist, NISCAIR, CSIR, New Delhi. A voucher specimen (no. PRL/JH/03/05) is deposited in the Herbarium of the Phytochemical Research Laboratory, Faculty of Pharmacy, Jamia Hamdard, New Delhi.

3.3. *Extraction and isolation*

The bark of *M. elengi* was dried in an oven at 45°C for 2–3 days and coarsely powdered. The ground bark (3 kg) was extracted with ethanol in a Soxhlet apparatus. The ethanol extract was concentrated under reduced pressure to yield a dark brown viscous mass (120 g, 4.0%). The extract was dissolved in a minimum amount of methanol and adsorbed on silica gel (60–120 mesh) for preparation of the slurry. The air-dried slurry was chromatographed over the silica gel column packed in petroleum ether (60–80°C). The column was eluted with petroleum ether, petroleum ether:chloroform (9:1, 3:1, 1:1, 1:3 v/v), chloroform, chloroform:methanol (99:1, 98:2, 95:5, 9:1, 3:1, 1:1, 1:3 v/v) and methanol successively, in order of increasing polarity, to isolate the following compounds.

Elengigallate (1): Elution of the column with chloroform:methanol (93:7) gave a pale brown amorphous powder of **1**, recrystallised from methanol; 115 mg (0.003%); R_f: 0.64 (toluene : ethyl acetate : formic acid; 5:4:1); m.p. 255–256°C; UV λ_{max} (MeOH): 215, 255 nm ($\log \varepsilon$ 4.8,2.7); IR υ_{max} (KBr): 3391, 3110, 2921, 2845, 1723, 1608, 1431, 1340, 1196, 1113, 1062, 1030, 970, 918, 870 and 757 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.28 (1H, d, $J = 2.5$ Hz, H-2), 7.25 (1H, d, $J = 2.5$ Hz, H-6), 6.93 (2H, m, H-2′, H-6′), 6.90 (2H, m, H-3′, H-5′), 6.88 (1H, m, H-4′), 3.55 (2H, brm, H_2-9′), 2.74 (2H, m, H_2-7′), 1.52 (2H, m, H_2-8′); ^{13}C NMR (DMSO-d_6): δ 141.31 (C-1), 110.40 (C-2), 145.22 (C-3), 158.74 (C-4), 148.17 (C-5), 111.48 (C-6), 167.49 (C-7), 151.99 (C-1′), 139.79 (C-2′), 107.10 (C-3′), 112.30 (C-4′), 120.48 (C-5′), 137.79 (C-6′), 29.04 (C-7′), 28.71 (C-8′), 60.76 (C-9′); +ve FABMS m/z (rel. int.): 288 $[M]^+$ ($C_{16}H_{16}O_5$) (71.3).

Acid hydrolysis: Compound **1** (20 mg) was dissolved in MeOH and 2 N HCl (1:1) and heated until half of the volume was left. The solution was extracted with EtOAc (3×10 mL), washed with water (2×10 mL), dried over Na_2SO_4 and evaporated to give 3-phenyl propanol; IR υ_{max} 3450 cm^{-1}. The aqueous phase was dried under reduced pressure, dissolved in methanol and crystallised to get needles of gallic acid, m.p. 235–238°C decomposition.

Mimusopstannin (2): Further elution of the column with chloroform:methanol (93:7) furnished a brown coloured amorphous powder of **2**, recrystallised from methanol; 110 mg (0.003%); R_f: 0.42 (toluene:ethyl acetate:formic acid; 5:4:1); m.p. 298–300°C (decomp.); UV λ_{max} (MeOH): 253 nm ($\log \varepsilon$ 5.7); IR υ_{max} (KBr): 3369, 3290, 3160, 2921, 2850, 1722, 1606, 1578, 1494, 1439, 1349, 1101, 1047 and 967 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.51 (2H, d, $J = 2.6$ Hz, H-2, H-6), 7.45 (2H, m, H-2‴, H-6‴), 7.39 (2H, m, H-3‴, H-5‴), 5.23 (1H, d, $J = 7.2$ Hz, H-1′), 5.01 (1H, d, $J = 7.1$ Hz, H-1″), 4.56 (2H, m, H-5′, H-5″), 4.47 (2H, m, H-2′, H-2″), 4.03 (1H, m, H-4″), 3.87 (1H, m, H-4′), 3.61 (2H, m, H-3′, H-3″), 3.46 (2H, brs, H_2-6′), 3.38 (2H, brs, H_2-6″), 2.73 (2H, m, H_2-7‴), 0.82 (3H, t, $J = 7.8$ Hz, Me-8).; ^{13}C NMR (DMSO-d_6): δ 146.09

(C-1), 139.66 (C-2), 159.06 (C-3), 152.58 (C-4), 148.09(C-5), 136.30 (C-6), 169.13 (C-7), 102.97 (C-1′), 71.78 (C-2′), 69.85 (C-3′), 69.28 (C-4′), 73.00 (C-5′), 65.84 (C-6′), 100.09(C-1″), 71.76 (C-2″), 69.28 (C-3″), 69.88 (C-4″), 75.50 (C-5″), 60.88 (C-6″), 158.57 (C-1‴), 114.16 (C-2‴), 112.85 (C-3‴), 141.44 (C-4‴), 111.42 (C-5‴), 110.16 (C-6‴), 18.2 (C-7‴), 8.9 (C-8‴); +ve FABMS *m*/*z* (rel. int.): 598 $[M]^+$ ($C_{27}H_{34}O_{15}$) (1.1), 127 (31.7).

Acid hydrolysis: Compound **2** (20 mg) was dissolved in MeOH and 2 N HCl (1:1) and heated until half of the volume was left. It was dried under reduced pressure and the residue was dissolved in methanol to separate gallic acid, m.p. 236–237°C. The residue was redissolved in water and analysed by paper chromatography along with standard samples of monosaccharides. Butanol:ethanol:water (4:1:2.2) was used as the developing solvent system. The paper was sprayed with aniline hydrogen phthalate. The sugar was identified as D-glucose.

Elengitannin (3): Further elution of the column with chloroform:methanol (93:7) afforded yellowish brown amorphous mass of **3**, recrystallised from methanol; 189 mg (0.006%); R_f: 0.68 (toluene:ethyl formate:formic acid; 10:10:3); m.p.: 286–287°C; UV λ_{max} (MeOH): 219, 253 nm (log ε 2.1,1.1); IR υ_{max} (KBr): 3435, 3260, 2922, 2846, 1722, 1610, 1583, 1495, 1440, 1348, 1210, 1102 and 1062 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.45 (2H, d, $J = 2.3$ Hz, H-2, H-6), 7.43 (2H, m, H-2a, H-6a), 7.40 (2H, m, H-3a, H-5a), 6.92 (1H, m, H-4a), 5.26 (1H, d, $J = 7.1$ Hz, H-1′), 4.96 (1H, d, $J = 6.9$ Hz, H-1″), 4.03 (2H, m, H-5′, H-5″), 3.83 (2H, m, H-2′, H-2″), 3.62 (1H, m, H-4″), 3.51 (2H, m, H-3′, H-3″), 3.49 (1H, m, H-4′) 3.43 (2H, brs, H_2-6′), 3.21 (2H, brs, H_2-1‴), 3.19 (2H, brs, H_2-1‴), 2.51 (2H, m, H-3‴, H-7″), 1.92 (2H, m, H_2-2‴), 1.21 (2H, m, H-4‴), 1.18 (4H, brs, H_2-5‴, H_2-6‴), 1.03 (3H, d, $J = 6.1$ Hz, Me-8‴), 0.79 (6H, brs, H_3-9‴, H_3-10‴); ^{13}C NMR: δ 141.32 (C-1), 140.07 (C-2), 158.68 (C-3), 148.19 (C-4), 152.03 (C-5), 139.74 (C-6), 167.49 (C-7), 107.14 (C-1′), 75.46 (C-2′), 70.05 (C-3′), 69.35 (C-4′), 76.81 (C-5′), 65.91 (C-6′), 102.94 (C-1″), 73.49 (C-2″), 69.35 (C-3″), 72.11 (C-4″), 76.81 (C-5″), 61.93 (C-6″), 60.90 (C-1‴), 31.47 (C-2‴), 36.84 (C-3‴), 29.29 (C-4‴), 29.29 (C-5‴), 22.21 (C-6‴), 34.38 (C-7‴), 18.93 (C-8‴), 13.78 (C-9‴), 11.51 (C-10‴), 148.19 ($C-1_a$), 112.29 ($C-2_a$), 111.32 ($C-3_a$), 108.76 ($C-4_a$), 110.27 ($C-5_a$), 112.00($C-6_a$); + ve FABMS *m*/*z* (rel. int.): 698 $[M]^+$ ($C_{34}H_{50}O_{15}$), 459 (10.2), 443 (12.6), 329 (17.8), 313 (11.5), 255 (22.6), 239 (19.2), 169 (21.3), 157 (26.2), 153 (29.8), 141 (24.8).

Acid hydrolysis: Compound **3** (20 mg) was dissolved in MeOH and 2 N HCl (1:1) and heated until half of the volume was left. The solution was dried under reduced pressure and the residue was dissolved in methanol to isolate gallic acid, m.p. 235–238°C. The residue was redissolved in water and analysed by paper chromatography along with standard samples of monosaccharides. Butanol:ethanol:water (4:1:2.2) was used as the developing solvent system. The paper was sprayed with aniline hydrogen phthalate. The sugar was identified as D-glucose.

Gallic acid diglucoside (4): Elution of the column with chloroform:methanol (23:2) afforded a colourless amorphous powder of **4**, recrystallised from methanol; 100 mg (0.003%); R_f: 0.78 (toluene:ethyl acetate:formic acid; 5:4:1); m.p. 310–312°C; UV λ_{max} (MeOH): 253 nm (log ε 6.3); IR υ_{max} (KBr): 3366, 3210, 3060, 2928, 2850, 1723, 1606, 1581, 1494, 1429, 1360, 1187, 1102, 1058, 975, 914 and 755 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.52 (1H, d, $J = 3.0$ Hz, H-2), 7.44 (1H, d, $J = 3.0$ Hz, H-6), 4.99

(1H, d, $J = 6.6$ Hz, H-1′), 4.96 (1H, d, $J = 6.6$ Hz, H-1″), 4.04 (2H, m, H-5′, H-5″), 3.86 (1H, m, H-2′), 3.84 (1H, m, H-2″), 3.40 (4H, m, H-3′, H-3″, H-4′, H-4″), 3.38 (2H, brs, H_2-6′), 3.28 (2H, brs, H_2-6″); ^{13}C NMR (DMSO-d_6): 139.85 (C-1), 138.62 (C-2), 158.64 (C-3), 162.98 (C-4), 152.62 (C-5), 111.36 (C-6), 170.12 (C-7), 110.22 (C-1′), 73.00 (C-2′), 64.84 (C-3′), 69.26 (C-4′), 75.50 (C-5′), 65.84 (C-6′), 102.89 (C-1″), 73.09 (C-2″), 69.31 (C-3″), 69.26 (C-4″), 75.50 (C-5″), 60.90 (C-6″); FAB-MS m/z (rel. int.): 494 $[M]^+$ ($C_{19}H_{26}O_{15}$).

Acid hydrolysis: Compound **4** (20 mg) was dissolved in MeOH and 2 N HCl (1:1) and heated until half of the volume was left. The solution was dried under reduced pressure and the residue was dissolve in methanol to separate gallic acid, m.p. 236–239°C. The residue was dissolved in water and analysed by paper chromatography along with standard samples of monosaccharides. Butanol:ethanol:water (4:1:2.2) was used as the developing solvent system. The paper was sprayed with aniline hydrogen phthalate. The sugar was identified as D-glucose.

Gallic acid phenoxy diglucoside (5): Further elution of the column with chloroform:methanol (23:2) afforded a pale brown amorphous powder of **5**, recrystallised from methanol; 800 mg (0.026%); R_f: 0.64 (toluene:ethyl formate: formic acid; 10:10:3); m.p. 187–188°C; UV λ_{max} (MeOH): 259 nm ($\log \varepsilon$ 5.2); IR υ_{max} (KBr): 3362, 3310, 3260, 2930, 2850, 1722, 1611, 1494, 1332, 1196, 1104 and 1027 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.51 (1H, d, $J = 2.7$ Hz, H-2), 7.44 (1H, d, $J = 2.7$ Hz, H-6), 6.92 (2H, m, H-2‴, H-6‴), 6.88 (2H, m, H-3‴, H-5‴), 5.48 (1H, d, $J = 7.0$ Hz, H-1″), 4.94 (1H, d, $J = 7.2$ Hz, H-1′), 4.53 (2H, m, H-5′, H-5″), 4.45 (2H, m, H-2′, H-2″), 4.04 (1H, m, H-4″), 3.91 (1H, m, H-4′), 3.63 (2H, m, H-3′, H-3″), 3.40 (1H, d, $J = 10.8$ Hz, H_2-6a), 3.36 (1H, d, $J = 10.8$ Hz, H_2-6′b), 3.32 (1H, d, $J = 10.1$ Hz, H_2-1″a), 3.28 (1H, d, $J = 10.1$ Hz, H_2-1″b), 2.51 (2H, m, H_2-7‴), 0.92 (2H, brs, H_2-8‴), 0.87 (2H, brs, H_2-9‴), 0.62 (3H, t, $J = 6.5$ Hz, Me-10‴); ^{13}C NMR (DMSO-d_6): δ 141.76 (C-1), 136.12 (C-2), 152.65 (C-3), 120.43 (C-4), 167.43 (C-5), 111.36 (C-6), 171.66 (C-7), 100.10 (C-1′), 73.16 (C-2′), 69.44 (C-3′), 66.01 (C-4′), 76.90 (C-5′), 63.19 (C-6′), 103.12 (C-1″), 72.58 (C-2″), 70.02(C-3″), 71.94 (C-4″), 76.81 (C-5″), 61.07 (C-6″), 158.31 (C-1‴), 115.89 (C-2‴), 112.85 (C-3‴), 141.03 (C-4‴), 110.18 (C-5‴), 108.71 (C-6‴), 33.16 (C-7‴), 29.15 (C-8‴), 28.98 (C-9‴), 17.99 (C-10‴); +ve FABMS m/z (rel. int.): 626 $[M]^+$ ($C_{29}H_{38}O_{15}$).

Acid hydrolysis: Compound **5** (20 mg) was dissolved in MeOH and 2 N HCl (1:1) and heated until half of the volume was left. The solution was dried under reduced pressure and the residue was dissolved in methanol to separate gallic acid, m.p. 237–239°C. The residue was redissolved in water and analysed by paper chromatography along with standard samples of monosaccharides. Butanol:ethanol:water (4:1:2.2) was used as the developing solvent system. The paper was sprayed with aniline hydrogen phthalate. The sugar was identified as D-glucose.

Elengibenzyl diglycoside (6): Elution of the column with chloroform:methanol (9:1) afforded a brown amorphous mass of **6**, recrystallised from methanol; 98 mg (0.003%); R_f: 0.62 (toluene:ethyl formate:formic acid; 10:10:3); m.p. 288–290°C; UV λ_{max} (MeOH): 216, 256 nm ($\log \varepsilon$ 2.1,6.2); IR υ_{max} (KBr): 3384, 3280, 2921, 2851, 1722, 1606, 1496, 1438, 1364, 1175, 1100 and 1033 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.58 (1H, d, $J = 2.5$ Hz, H-2), 7.51 (1H, d, $J = 2.5$ Hz, H-6), 5.54 (1H, d, $J = 7.1$ Hz, H-1″), 5.01 (1H, d, $J = 7.2$ Hz, H-1′), 4.09 (1H, brm, H-5′), 4.05 (1H, m, H-5″), 3.89

(2H, m, H-2′, H-2″), 3.87 (2H, m, H-3‴, H-3″), 3.48 (2H, m, H-4′, H-4″), 3.38 (2H, brs, H_2-6′), 1.20 (3H, d, $J = 6.2$ Hz, Me-6″); ^{13}C NMR (DMSO-d_6):139.70 (C-1), 111.83 (C-2), 158.65 (C-3), 148.13 (C-4), 152.70 (C-5), 110.19 (C-6), 169.11 (C-7), 102.97 (C-1′), 73.06 (C-2′), 65.96 (C-3′), 68.05 (C-4′), 75.54 (C-5′), 63.08 (C-6′), 100.12 (C-1″), 73.03 (C-2″), 65.37 (C-3″), 68.15 (C-4″), 75.54 (C-5″), 17.88 (C-6″); +ve FABMS *m*/*z*: 480 $[M]^+$ ($C_{19}H_{26}O_{14}$).

Acid hydrolysis: Compound **6** (20 mg) was dissolved in MeOH and 2 N HCl (1:1) and heated until half of the volume was left. The solution was dried under reduced pressure and the residue was dissolved in methanol to separate gallic acid, m.p. 234–237°C. The residue was redissolved in water and analysed by paper chromatography along with standard samples of monosaccharides. Butanol:ethanol:water (4:1:2.2) was used as the developing solvent system. The paper was sprayed with aniline hydrogen phthalate. The sugars were identified as D-glucose and D-rhamnose.

Gallic acid triphenoxy diglycoside (7): Further elution of the column with chloroform:methanol (9:1) yielded a light amorphous powder of **7**, recrystallised from methanol; 123 mg (0.004%); R_f: 0.63 (toluene:ethyl formate:formic acid; 10:10:3); m.p. 239–240°C; UV λ_{max} (MeOH): 253, 356 nm (log ε 5.2,1.3). IR ν_{max} (KBr): 3480, 3396, 3285, 2919, 2850, 1723, 1607, 1493, 1439, 1350, 1187, 1104, 1050 and 968 cm^{-1}; ^{1}H NMR (DMSO-d_6): δ 7.98 (1H, d, $J = 2.3$ Hz, H-2), 7.86 (1H, m, H-6a), 7.82 (2H, m, H-2b, H-6b), 7.69 (1H, d, $J = 2.3$ Hz, H-6), 7.34 (2H, m, H-2c, H-6c), 7.34 (2H, m, H-3a, H-5a), 7.04 (2H, m, H-3b, H-5b), 6.87 (2H, m, H-3c, H-5c), 6.73 (3H, brm, H-4a, H-4b, H-4c), 5.17 (1H, d, $J = 7.1$ Hz, H-1′), 5.12 (1H, d, $J = 7.0$ Hz, H-1″), 4.29 (2H, m, H-5′, H-5″), 4.16 (2H, m, H-2′, H-2″), 3.87 (2H, m, H-3′, H-3″), 3.81 (1H, m, H-4″) 3.72 (1H, m, H-4′), 3.35 (2H, brs, H_2-6′), 1.30 (3H, d, $J = 6.5$ Hz, Me-6″); ^{13}C NMR (DMSO-d_6): oC 148.09 (C-1), 140.13 (C-2), 158.49 (C-3), 158.48 (C-4), 158.48 (C-5), 139.57 (C-6), 169.13 (C-7), 152.64 (C-1a), 141.57 (C-2a), 111.03 (C-3a), 139.57 (C-4a), 114.13 (C-5a), 146.94 (C-6a), 152.00 (C-1b), 146.43 (C-2b), 110.24 (C-3b), 135.89 (C-4b), 135.92 (C-5b), 141.13 (C-6b), 152.64 (C-1c), 144.10 (C-2c), 139.57 (C-3c), 135.89 (C-4c), 111.45 (C-5c), 140.01 (C-6c), 103.01 (C-1′), 73.08 (C-2′), 69.94 (C-3′), 69.36 (C-4′), 75.48 (C-5′), 60.91 (C-6′), 100.13 (C-1″), 73.08 (C-2″), 69.36 (C-3″), 71.89 (C-4″), 75.48 (C-5″), 17.94 (C-6); +ve FABMS *m*/*z*: 706 $[M]^+$ ($C_{37}H_{38}O_{14}$), 391 (19.6), 315 (70.5), 153 (25.2), 125 (21.3).

Acid hydrolysis: Compound **7** (20 mg) was dissolved in MeOH and 2 N HCl (1:1) and heated until half of the volume was left. The solution was dried under reduced pressure and the residue was dissolved in methanol to separate gallic acid, m.p. 235–237°C. The residue was redissolved in water and analysed by paper chromatography along with standard samples of monosaccharides. Butanol:ethanol:water (4:1:2.2) was used as the developing solvent system. The paper was sprayed with aniline hydrogen phthalate. The sugars were identified as D-glucose and D-rhamnose.

Acknowledgements

The authors are thankful to the Head, Regional Sophisticated Center, Central Drug Research Institute, Lucknow for recording spectral data of the compounds.

References

Anonymous. (2003). *The wealth of India, a dictionary of Indian raw materials and industrial products* (Vol. VI, pp. 383–385). New Delhi: CSIR, PID.

Banerji, R., Prakash, D., Patnaik, G.K., & Nigam, S.K. (1982). Spasmolytic activity of saponins. *Indian Drugs, 20*, 51–54.

Dar, A., Behbahanian, S., Malik, A., & Jahan, N. (1999). The methanol extract of *M. elengi* caused hypotensive activity in anaesthetized rats. *Phytomedicine, 6*, 373–378.

Drury, H. (1873). *The useful plants of India with notices of their chief value in commerce, medicine and the arts* (2nd ed., pp. 292–293). London: W.H. Allen & Co.

Jahan, N., Malik, A., Mustafa, G., Ahmad, Z., Ahmad, S., Anis, E., et al. (2001). Triterpenes from *Mimusops elengi* Linn. *Natural Product Letters, 15*, 177–185.

Kirtikar, K.R., & Basu, B.D. (1993). *Indian medicinal plants* (Vol. II, pp. 1944–1946). Allahabad: Lalit Mohan Basu Prakashan.

Misra, G., Nigam, S.K., & Mitra, C.R. (1974). Studies on *Mimusops* species. *Planta Medica, 26*, 155–165.

Mundhada, S.S., & Takte, P.A. (2005). Preliminary phytochemical investigation and antimicrobial activity of fruits of *Mimusops elengi* Linn. *Indian Drugs – Bombay, 42*, 417–423.

Sahu, N.P., Mandal, N.B., Banerjee, S., & Siddiqui, K.A.I. (2001). Chemistry and biology of the triterpenes and saponins from seeds of *Mimusops elengi*. *Journal of Herbs, Spices & Medicinal Plants, 8*, 29–37.

Shah, P.J., Gandhi, M.S., Shah, M.B., Goswami, S.S., & Santani, D. (2003). Study of *Mimusops elengi* in experimental gastric ulcers. *Journal of Ethnopharmacology, 89*, 305–311.

Varshney, I.P., & Logani, K.M. (1969). Study of saponins and sapogenins from *Mimusops elengi* Linn. *Indian Journal of Applied Chemistry, 32*, 173–176.