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Coumaroyl triterpene lactone, phenolic and naphthalene glycoside from stem bark of *Diospyros angustifolia* ☆

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Abstract

From the ethanolic extract of stem bark of *D. angustifolia* three new compounds, a coumaroyl triterpene lactone, diospyrosooleanolide (**1**), a phenolic glycoside, diospyrososide (**2**) and a naphthalene glycoside, diospyrosonaphthoside (**3**) were isolated along with five known compounds (**4–8**). The structures of these compounds were established on the basis of spectroscopic and chemical evidences.

Keywords: *Diospyros angustifolia*; Ebinaceae; Diospyrosoleanolide; Phenolic glycoside

1. Introduction

Diospyros angustifolia (Miq.) Kost syn: *Diospyros nigrescenas* (Dalz.) Suldanha, *Maba angustifolia* Miq. belongs to the family Ebinaceae and is a tropical tree found in Western Ghats from Concan to Mysore in India. Genus *Diospyros* constitutes more than 350 species some of which are known for the treatment of diseases in traditional systems of medicine such as Ayurveda, the African folklore and Chinese medicine. Due to their medicinal importance, various groups have examined the chemical constituents of different species of *Diospyros* and reported diverse compounds including hydrocarbons, terpenes, naphthoquinones and naphthalene based aromatic compounds (Mallavadhani et al., 1998). *D. angustifolia* was collected in general biological screening programme of CDRI for detail chemical examination. In present paper we wish to report the isolation and structural elucidation of three new compounds **1–3** (Fig. 1). To the best of our knowledge no phytochemical work has been reported on this plant species.

2. Result and discussion

The ethanolic extract of *D. angustifolia* was resolved into the *n*-hexane, chloroform, *n*-butanol and aqueous fractions. On repeated chromatographic separation the chloroform fraction afforded a new compound (**1**) along with five known compound (**4–8**) and *n*-butanol fraction afforded two new compounds (**2–3**). Characterization of the known compounds was carried out by direct comparison of their physicochemical data with those reported in literature. The structures of new compounds are established as follows.

Compound **1** was obtained as white amorphous powder, which gave a positive Libermann–Burchard test for triterpenes. ES-MS and FAB-MS of compound **1** showed pseudomolecular ion peak at $[M+H]^+$ 619 and $[M+Na]^+$ 641 corresponding to molecular formula $C_{39}H_{54}O_6$, consistent with the ^{13}C and ^1H NMR spectra. Its IR displayed absorption bands attributable to a hydroxyl group (3435 cm^{-1}), γ-lactone (1755 cm^{-1}) and a conjugated ester carbonyl (1703 cm^{-1}). The ^1H NMR spectrum in C_5D_5N showed signals for seven tertiary

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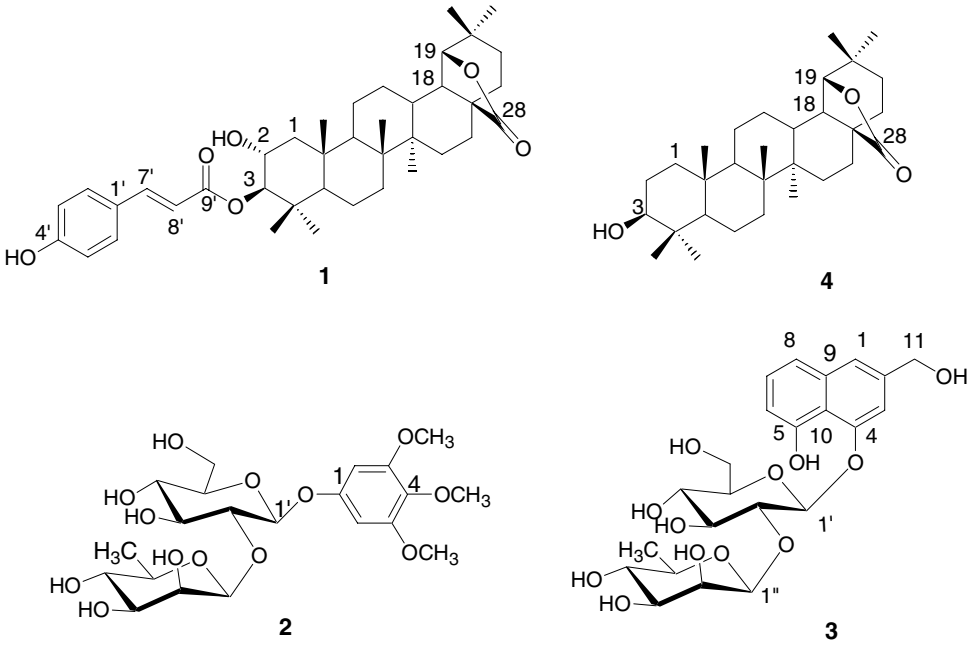

Fig. 1.

methyl signal in the region δ 0.78–1.03 indicating the triterpenoidal nature of compound, two olefin protons at δ 6.68, 8.00 (1H each, d, $J = 15.8$ Hz) and aromatic protons at δ 7.17, 7.56 (2H each, merged with pyridine signal) which were clearly seen at δ 6.79, 7.44 (2H each, d, $J = 8.6$ Hz) as A_2B_2 system when spectrum was recorded in DMSO-d_6 indicating presence of *p*-coumaroyl moiety. Presence of this moiety was further confirmed by ^{13}C NMR (Table 1). In addition to these protons, three oxymethine protons appeared at δ 4.03 (1H, s), 4.34 (1 H, ddd, $J = 11.4$, 9.8, 4.6 Hz), and 5.22 (1H, d, $J = 9.8$ Hz). The proton at δ 4.03 was assigned to H-19 by comparison with known compound **4** (Yoshihira et al., 1971). ^{1}H–^{1}H COSY revealed that other two oxymethine proton at δ 4.34 and 5.22 were vicinal. On the basis of chemical shift, multiplicities (Kojima and Ogura, 1989), as well as biogenetic considerations, signal at δ 5.22 was assigned to H-3α and at δ 4.34 to H-2β. Further downfield shift of H-3α proton indicated that the 3-β hydroxyl group was esterified with coumaroyl moiety. Additionally, the ^{13}C chemical shift values of **1** (Table 1) were very similar to with those of known olean lactone **4** except for C-1, C-2 and C-3 which appeared downfield at δ 48.5, 66.3, 85.7, respectively. These data indicates that the compound **1** had a hydroxyl group at position C-2 and coumaroyl ester moiety at C-3. On the basis of these evidences compound **1** was identified as 2α-hydroxy-3β-trans-*p*-coumaroyl-28,19β-oleanolide, is a new compound, named as diospyrosooleanolide.

Compound **2** obtained as white amorphous powder, gave postive Fiegel test for glycosides. Its FAB-MS showed peak at 493 $[M + H]^+$ and 515 $[M + Na]^+$ corresponding to molecular formula $C_{21}H_{32}O_{13}$. The UV spectrum exhibited the absorption band at 215 and 269 nm and IR spectrum displayed an absorption bands for hydroxyl group (3407 cm^{-1}), and aromatic ring (1602 and 1508 cm^{-1}). On acid hydrolysis compound **2** afforded two sugars, identified as glucose and rhamnose by co-TLC with authentic samples. The ^{1}H NMR spectrum of **2** assigned with the aid of ^{1}H–^{1}H COSY showed two aromatic proton signals at δ 6.45 (2H, s), three proton signals at δ 3.80 ($2 \times OCH_3$) and 3.69 (OCH_3), two anomeric proton signals at δ 5.58 (d, $J = 1.5$ Hz), 4.89 (d, $J = 7.5$ Hz) for rhamnose and glucopyranose, respectively, 4.13 (1H, dq, $J = 6.3, 9.6$ Hz), 1.32 (3H, d, $J = 6.3$ Hz) which is a characteristics of rhamnose H-5$''$ and H-6$''$, respectively, and δ 3.93 (1H, dd, $J = 1.5$, 3.3 Hz) for rhamnose H-2$''$, whereas other sugar proton signals appeared in the δ 3.30–3.69 region as multiplets. The coupling constants of anomeric protons indicated β-configuration of glucopyranosyl and α-configuration of rhamnopyranosyl moieties. The ^{13}C NMR data (Table 2) exhibited one methoxyl carbon signal at δ 61.2 (characteristic of *ortho*-disubtituted OCH_3), two methoxyl carbon signal at δ 56.6, two anomeric carbon at δ 101.5 (C-1$'$), 102.2 (C-1$''$), one methyl at 18.2 (C-6$''$) along with other aromatic and sugar carbons. The ^{1}H and ^{13} C chemical shift values of aglycon portion were similar to those of the known compound, 1[α-L-rhamnosyl(1 $\rightarrow$ 6)-β-D-glucopyranosyloxy]-3,4,6-trimethoxy benzene (Andrianaivoravelona et al., 1999) but differ considerable in sugar carbon signals, particularly C-1$'$ and C-2$'$ of glucose moiety. The C-2$'$ of glucose moiety appeared down field and C-1$'$ upfield due to

Table 1
^{13}C NMR spectral data of compounds **1** and **4**

Position	Compound **1**,C_5H_5N δ_C	Compound **4**, $CDCl_3$ δ_C
1	48.5	38.9
2	66.3	27.3
3	85.7	78.8
4	39.5	40.5
5	55.1	55.4
6	18.2	18.2
7	33.6	33.7
8	39.9	40.7
9	51.1	51.2
10	38.2	37.2
11	21.0	20.8
12	25.7	25.5
13	36.2	35.9
14	40.5	38.8
15	28.5	27.8
16	26.2	26.4
17	49.5	46.0
18	46.5	46.6
19	84.7	85.9
20	33.4	33.5
21	31.2	31.9
22	32.5	32.2
23	23.4	23.9
24	13.5	13.6
25	14.8	25.4
26	17.6	15.3
27	17.7	16.4
28	179.8	179.8
29	28.5	28.7
30′	28.5	27.9
1′	123.6	–
2′, 6′	130.4	–
3′, 5′	116.5	–
4′	161.1	–
7′	144.6	–
8′	115.8	–
9′	167.8	–

glycosidation effect (Agrawal and Bansal, 1989). This indicated that rhamnopyranosyl moiety was linked at C-2′ of glucopyranosyl moiety which was further confirmed by ^1H NMR of acetate derivative, **2a** (Table 2) in which no considerable change in chemical shift of H-2′ proton was observed. Thus, on the basis of above spectral and chemical evidences compound **2** was identified as 1[α-L-rhamnosyl(1 → 2)-(β-D-glucopyranosyloxy)]-3,4,5-trimethoxy benzene, which was a new compound named as diospyrososide.

Compound **3** was obtained as amorphous powder, gave positive phenolic test and Fiegel test for glycoside indicating compound to be a phenolic glycoside. The ES-MS and FAB-MS of the compound showed peak at m/z 499 $[M+H]^+$ and 521 $[M+Na]^+$ corresponding to molecular formula $C_{23}H_{30}O_{12}$. The UV spectrum exhibited band at 224 and 297 nm and IR spectrum showed absorption bands for hydroxyl (3434 cm^{-1}) and for aromatic ring (1625, 1591 cm^{-1}). On acid hydrolysis compound **3** afforded two sugars, identified as glucose and rhamnose by co-TLC with authentic samples. The ^1HNMR spectrum (Table 3) of **3** revealed aromatic proton at δ 7.50 (1H, d, $J = 1.0$ Hz, H-1), 7.19 (1H, d, $J = 1.0$ Hz, H-3) AX system, δ 7.35 (2H, m, H-6, H-8), 6.82 (1H, dd, $J = 5.4$, 3.2 Hz, H-7) ABC system, oxymethylene proton at δ 4.78 (2H, s), two anomeric protons at 5.58 (1H, d, $J = 7.2$ Hz, H-1′) and 5.30 (1H, d, $J = 1.4$ Hz, H-1″). Other sugar protons appeared at δ 3.53–4.08. On acetylation compound 3 yielded an octaacetyl derivative **3a**. The ^1H NMR of octaaetate (**3a)** showed aromatic proton signals at δ 7.70 (1H, d, $J = 8.4$ Hz, H-6), 7.50 (1H, t, $J = 7.8$ Hz, H-7), 7.10 (1H, d, $J = 8.4$ Hz, H-8), 7.26 (brs, H-1), 7.12 (brs, H-3), anomeric protons at δ 5.34 (1H, d, $J = 7.8$ Hz, H-1′), 5.15 (1H, brs, H-1″), oxymethylene proton at δ 5.27 (s). These data indicated the presence of two sugar moieties and substituted naphthalene nucleus. The ^{13}C NMR data (Table 3) confirmed the above inference. Further, the anomeric carbon signals for glucose and rhamnose appeared at δ 101.6 and 103.7, respectively, indicating that both the sugar residues were in pyranose form. In differential nOe spectra (Fig. 2) of **3**, nOe was observed between the oxymethylene protons (H-11) and naphthalene H-1, H-3: the intensity of the H-1 (δ 7.50) and H-3 (δ 7.19) signals were increased on irradiation of the oxymethylene proton signal (δ 4.78) indicating oxymethylene group is located at C-2 of naphthalene. Further nOe was observed between glucose H-1′ and naphthalene H-3, glucose H-2′ and the rahmnose H-1″: the intensity of the H-3 (δ 7.19) signal of naphthalene was increased on irradiation of the glucose H-1′ (δ 5.58) and intensity of the glucose H-2′ (δ 3.81) was increased on irradiation of rhamnose H-1″ (δ 5.30) indicating glucose moiety was involved in glycosidation with naphthalene nucleus at C-4 hydroxyl group and rhamnose was linked at C-2′ of glucose moiety. The position of rhamnose was confirmed by ^{13}C NMR chemical shift in which C-2 of glucose experienced down field shift and C-1 experienced upfield shift (Agrawal and Bansal, 1989). This was also supported by ^1H NMR of its acetate derivative **3a** in which no considerable chemical shift of H-2 of glucose was observed. On the basis of above spectral and chemical evidences compound **3** was identified as 4[α-L-rhamnosyl(1 → 2)-β-D-glucopyranosyloxy]-2-hydroxymethylene,5-hydroxy naphthalene, which is a new compound, named as diospyroso-naphthoside.

In addition to these three new compounds five known compounds viz. 3-β-hydroxy-28,19β-oleanolide **(4)** (Yoshihira et al., 1971), betulinic acid (**5**) (Sholichin et al., 1980), lupeol (**6**) (Sholichin et al., 1980), β-amyrin (**7**) (Takahashi et al., 1999) and friedline (**8**) (Kalass and Tinto, 1992) were also isolated and characterized by direct comparison of their physicochemical data with those reported in literature. Out of these compounds, betulinic acid is the major constituent (5.7% of the

Table 2
NMR spectral data of compounds **2** and **2a**

Position	**2**	**2**	**2a**
	δ_H in CD_3OD	δ_C in CD3OD	δ_H in $CDCl_3$
Aglycon			
1	–	155.9	–
2,6	6.45 (s)	95.7	6.32 (s)
3,5	–	154.9	–
4	–	134.4	–
3,5-OCH_3	3.80 (s)	56.6	3.85 (s)
4-OCH_3	3.69 (s)	61.2	3.81 (s)
Glucose			
1′	4.89 (d, $J = 7.5$ Hz)	101.5	5.00 (d, $J = 7.8$ Hz)
2′	3.54–3.69 (m)	79.3	3.95 (t, $J = 9.3$ Hz)
3′	3.54–3.69 (m)	78.7	5.34 (t, $J = 9.3$ Hz)
4′	3.38–3.48 (m)	71.9	5.00–5.03 (m)
5′	3.33 (m)	78.3	3.85 (m)
6′a	3.54–3.69 (m)	62.7	4.26 (dd, $J = 5.7, 12.6$ Hz)
6′b	3.54–3.69 (m)		4.12 (m)
Rhamnose			
1″	5.28 (d, $J = 1.5$ Hz)	102.2	5.03 (brs)
2″	3.93 (dd, $J = 1.5, 3.3$ Hz)	72.3	5.00–5.03 (m)
3″	3.54–3.69 (m)	72.2	5.26 (dd, $J = 3.0, 10.2$ Hz)
4″	3.38–3.48 (m)	73.9	5.08 (t, $J = 9.9$ Hz)
5″	4.13 (dq, $J = 6.3, 9.6$ Hz)	69.9	4.23 (m)
6″	1.32 (d, $J = 6.3$ Hz)	18.2	1.20 (d, $J = 6.0$ Hz), 2.14, 2.10, 2.05, 2.03 (s, 3H each), 1.98 (s, 6H) (for six acetoxy methyl)

Table 3
NMR spectral data of compounds **3** and **3a**

Position	**3**	**3**	**3a**
	δ_H in CD_3OD	δ_C in CD_3OD	δ_H in CD_3Cl_3
Aglycon			
1	7.50 (d, $J = 1.0$ Hz)	120.7	7.26 (brs)
2	–	138.6	–
3	7.19 (d, $J = 1.0$ Hz)	109.9	7.12 (brs)
4	–	155.3	–
5	–	155.0	–
6	7.35 (m)	112.0	7.70 (d, $J = 8.4$ Hz)
7	6.82 (dd, $J = 5.4, 3.2$ Hz)	129.1	7.50 (t, $J = 7.8$ Hz)
8	7.35 (m)	122.0	7.10 (d, $J = 8.4$ Hz)
9	–	141.6	–
10	–	116.0	–
11	4.78 (s)	65.5	5.27 (s)
Glucose			
1′	5.58 (d, $J = 7.2$ Hz)	101.6	5.34 (d, $J = 7.8$ Hz)
2′	3.81 (overlapped t, $J = 7.2$ Hz)	81.9	4.00 (t, $J = 9.6$ Hz)
3′	3.68–3.78 (m)	79.1	5.43 (t, $J = 9.6$ Hz)
4′	3.68–3.78 (m)	71.6	5.13 (*m*)
5′	3.53 (m)	78.9	3.77 (m)
6′a	3.90 (brd, $J = 11.0$ Hz)	62.7	4.29 (dd, $J = 4.5, 12.6$ Hz)
6′b	3.68–3.78 (m)		4.05 (dd, $J = 2.5, 12.6$ Hz)
Rhamnose			
1″	5.30 (d, $J = 1.4$ Hz)	103.7	5.15 (brs)
2″	4.08 (m)	72.7	5.13 (m)
3″	3.68–3.78 (m)	72.5	5.16 (dd, $J = 3.3$, 9.9 Hz)
4″	3.53 (m)	74.3	4.96 (t, $J = 9.9$ Hz)
5″	3.68–3.78 (m)	71.0	3.83 (m)
6″	1.07 (d, $J = 6.2$ Hz)	18.0	0.90 (d, $J = 6.3$ Hz), 2.40, 2.17, 2.04, 2.00, 1.97, 1.80 (s, 3H each), 2.12 (s, 6H) (for eight acetoxy methyl)

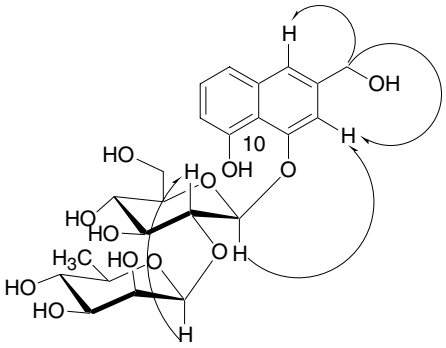

Fig. 2. nOe correlation of **3**.

ethanolic extract). Thus this plant constitutes an important source of betulinic acid.

3. Experimental

3.1. General

Melting points were recorded on a Complab melting point apparatus and are uncorrected. IR spectra (KBr) were recorded on a Perkin–Elmer RX-1 spectrophotometer. UV spectra were obtained on a Perkin Elmer λ-15 UV spectrophotometer. NMR spectra were run on an AVANCE DPX 200 and Bruker DRX 300 spectrometers; FAB MS were recorded on Jeol SX 102/DA-6000 mass spectrometer. ESMS on Micromass Quattro II. Elemental analyses were obtained in a Carlo-Erba-1108 CHN elemental analyzer. Column chromatography was performed using silica gel (60–120 and 230–400 mesh).

3.2. Plant material

Diospyros angustifolia stem bark was collected from Sindhu Durg, Maharastra, India, in February 1997. The collection and authentification were made by Botany Division of CDRI where voucher specimen (No. 8018) is preserved.

3.3. Extraction and isolation

Air dried and powdered *D. angustifolia* stem bark (8 kg) was extracted at room temperature with EtOH (4 × 20 l). The EtOH extract evaporated to dryness, was then fractionated successively with *n*-hexane, $CHCl_3$, *n*-BuOH, and water. The $CHCl_3$ fraction was subjected to CC over silica gel column (60–120 mesh) using $CHCl_3$ containing increasing amount of MeOH as eluent afforded 250 ml × 40 fractions which were grouped in to 7 fractions (F-1 to F-7). CC of F-6 using $CHCl_3$ containing increasing amount of MeOH afforded **1** (15 mg) and F-5 afforded **5** (20 g). On similar purification using *n*-hexane:acetone gradient, F-3 afforded **4** (190 mg), F-4 afforded **6** (2.3 g), F-2 afforded **7** (130 mg) and F-1 afforded **8** (335 mg). The *n*-BuOH fraction was subjected to column chromatography over silica gel (60–120 mesh) column, using EtOAc saturated with water containing increasing amount of MeOH as eluent yielding 500 ml × 50 fraction, which were reduced to 10 fractions after comparison of TLC (F-8 to F-17). Flash CC (230–400 mesh) of F-13 using $CHCl_3$ containing increasing amount of MeOH and water as eluent afforded **2** (500 mg); similar purification of F-14 afforded **3** (120 mg).

3.4. 2α-Hydroxy-3β-trans-p-coumaroyl-28,19β-oleanolide, diospyrosooleanolide (*1*)

White amorphous powder; $[\alpha]_D^{29}$: −16.6 (*c*, 0.102, C_5H_5N); UV (MeOH) λ_{max} nm: 202, 288, 323, 332; IR ν_{max} (KBr) cm^{-1}: 3435, 3136, 2939, 1755, 1703, 1610, 1386, 1265, 1081, 931. ^1H NMR (pyridine-d_5, 200 MHz) δ 8.0 (1H, d, $J = 15.8$ Hz, H-7′), 7.56 (2H, merge with solvent signal, H-2′ and H-6′), 7.17 (2H, merge with solvent peak, H-3′ and H-5′), 6.68 (1H, d, $J = 15.8$ Hz, H-8′), 5.22 (1H, d, $J = 9.8$ Hz, H-3), 4.34 (1H, ddd, $J = 11.4$, 9.8, 4.6 Hz, H-2), 4.03 (1H, s, H-19), 1.03 (9H, s), 0.91 (6H, s), 0.85 (3H, s),0.78 (3H, s); ^1H NMR (DMSO-d_6, 200 MHz) δ 7.53 (1H, d, $J = 15.8$ Hz, H-7′), 7.44 (2H, d, $J = 8.6$ Hz, H-2′, H-6′), 6.79 (2H, d, $J = 8.6$ Hz, H-3′, H-5′), 6.32 (1H, d, $J = 15.8$ Hz, H-8′), 4.51 (2H, m, H-3, H-2), 3.95 (1H, s, H-19), 0.97 (3H, s), 0.96 (3H, s), 0.92 (3H, s), 0.90 (3H, s), 0.88 (3H, s), 0.86 (3H, s), 0.82 (3H, s); ^{13}C NMR (pyridine-d_5, 50 MHz) see Table 1; FAB MS (pos.): m/z 619 $[M+H]^+$, 641 $[M+Na]^+$, ES-MS (pos.): m/z 619 $[M+H]^+$, 641 $[M+Na]^+$. Elemental analysis: calc. for $C_{39}H_{54}O_6$: C, 75.69%, H, 8.80%. Found: C, 75.71%, H, 8.89%.

3.5. 1[α-L-Rhamnosyl(1 → 2)-(β-D-glucopyranosyloxy)]-3,4,5-trimethoxy benzene (*2*)

White amorphous powder; $[\alpha]_D^{27}$: −80.0 (*c*, 0.12, MeOH); UV (MeOH) λ_{max} nm: 215, 269; IR ν_{max} (KBr) cm^{-1}: 3407, 2927, 1657, 1602, 1508, 1459, 1420, 1230, 1137, 1076, 827. ^1H NMR (CD_3OD, 300 MHz) see Table 1, ^{13}C NMR (CD_3OD, 75 MHz) see Table 1; FAB MS (pos.): m/z 493 $[M+H]^+$, 515 $[M+Na]^+$. Elemental analysis: calc. for $C_{21}H_{32}O_{13}$: C, 51.22%, H, 6.55%. Found: C, 51.27%, H, 6.59%.

3.6. Acetylated derivative (*2a*)

Compound **2** (10 mg) was dissolved in pyridine (0.5 ml) and Ac_2O (0.5 ml) was added. The mixture was left at room temperature overnight. After workup **2a** (10.2 mg) was obtained as amorphous powder. ^1H NMR 300 MHz ($CDCl_3$): see Table 1; FAB MS (pos.): m/z 745 $[M+H]^+$.

3.7. 4[α-L-Rhamnosyl(1 → 2)-β-D-glucopyranosyloxy]-2-hydroxymethylene,5-hydroxy naphthalene, diospyrosonaphthoside (**3**)

White amorphous powder; $[\alpha]_D^{27}$: −119.0 (*c*, 0.17, MeOH) UV (MeOH) λ_{max} nm: 224, 297; IR ν_{max} (KBr) cm^{-1}: 3434, 2928, 1625, 1591, 1389, 1255, 1420, 1230, and 1069. ^1H NMR (CD_3OD, 200 MHz) see Table 3, ^{13}C NMR (CD_3OD, 50 MHz) see Table 3; FAB MS (pos.): *m/z* 499 $[M + H]^+$, 521 $[M + Na]^+$; ES MS $[M + H]^+$, 521 $[M + Na]^+$; 537 $[M + K]^+$, 190 $[M + sugar]^+$. Elemental analysis: calc. for $C_{21}H_{32}O_{13}$: C, 55.42%, H, 6.07%. Found: C, 55.40%, H, 6.01%.

3.8. Acetylated derivative (**3a**)

Compound **3** (10 mg) was dissolved in pyridine (0.5 ml) and Ac_2O (0.5 ml) was added. The mixture was left at room temperature overnight. After workup **3a** (10.4 mg) was obtained as amorphous powder. ^1H NMR 300 MHz ($CDCl_3$): see Table 1; FAB MS (pos.): *m/z* 835 $[M + H]^+$.

3.9. Hydrolysis of compounds **2** and **3**

The solution of compound **2** or **3** (5.0 mg) in 2 N HCl in 80% of ethanol (0.5 ml) was refluxed for 3h. After this, water was added in the reaction mixture and ethanol was evaporated, it was again refluxed for one more hour. Reaction mixture was then extracted with chloroform; the aqueous phase was neutralized with Amberlite IR 410 CO_3^{2-} resin, filtered and concentrated to give mixtures of sugar. The sugar was identified as glucospyranose and rhamnose by co-TLC with authentic samples.

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