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ORIGINAL ARTICLE

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Four glucosides of *p*-hydroxyphenyl derivatives from birch leaves

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Abstract The extractive of shirakamba (*Betula platyphylla* Sukatchev var. *japonica* Hara) leaves was investigated. Four glucosides of *p*-hydroxyphenyl derivatives were isolated, and their structures were indentified as betuloside (I), 3,4′-dihydroxy-propiophenone-3-*β*-D-glucopyranoside (II), salidroside (III), and arbutin (IV). Arbutin was newly found in the leaves of shirakamba.

Key words Phenolic glucoside · Leaves · Birch · *Betula platyphylla* Sukatchev var. *japonica* Hara

Introduction

In a previous paper[1] we reported the isolation of two lignan rhamnosides in the extractives of the leaves of shirakamba (*Betula platyphylla* Sukatchev var. *japonica* Hara; Betulaceae) and described their structures. In a further study of the extractives of the leaves of the constituents, four glucosides of phenolic compounds were isolated. In a structural explanation of the four phenolic glucosides is provided in this paper (Fig. 1).

Results and discussion

Compound I was positive in diazotized sulfanilic acid (DSA), showing that it was a phenolic compound. The M^+ of compound I was observed at m/z 328, and the acetyl derivative of compound I (IA) gave M^+ at m/z 538. The mass difference between the two molecular ions indicate that compound I has five free hydroxyl groups. The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of acetate IA (Table 1) showed an AA'BB' type double doublet at δ 7.19 (2H, d, J = 8.4 Hz) and 6.96 (2H, d, J = 8.4 Hz) assignable to four aromatic protons of $C_{2',6'}$ and $C_{3',5'}$, indicating the existence of a 1,4-disubstituted benzene ring in acetate IA. In the two-dimensional homonuclear chemical shift-correlated spectroscope (^{1}H-^{1}HCOSY) of acetate IA, a correlation between two methylene protons at C_1 [δ 2.69 (2H, m)] and C_2 [δ 1.84 (1H, m), 1.72 (1H, m)] and a methine proton C_3 [δ 3.76 (1H, m)] and methyl protons at C_4 [δ 1.12 (3H, d, J = 6.4 Hz)] was observed. A singlet at δ 2.27 was assigned to the methyl protons of an acetoxyl group on the aromatic ring. The alcoholic acetoxyl groups gave four singlets at δ 2.01, 2.03, 2.04, and 2.05.

On the other hand, the presence of a glucopyranosyl moiety in compound I was suggested by a carbon 13 nuclear magnetic resonance (^{13}C-NMR) analysis (Table 2), which showed six resonances at δ 103.7 (C-1″), 76.6 (C-2″), 79.6 (C-3″), 73.2 (C-4″), 79.2 (C-5″), and 64.3 (C-6″); and its acetyl derivative IA gave six signals at δ 99.2 (C-1″), 71.6 (C-2″), 73.0 (C-3″), 68.6 (C-4″), 71.7 (C-5″), and 62.1 (C-6″).[2–6] The mode of the glucosidic linkage was determined to be *β*-form based on the large coupling constant of the anomeric proton signal at δ 4.50 (1H, d, J = 7.9 Hz) in the ^{1}H-NMR spectrum of acetate IA. The long-range connectivities observed in the heteronuclear multiple bond correlation (HMBC) spectrum of acetate IA revealed a connection between the glucosyl residue and the aglycone. The anomeric proton signal at δ 4.50 correlated with the signal of C-3. This result shows that the glucosyl residue is linked to C-3.

Thus, it is concluded that compound I is 3-(4′-hydroxyphenyl) butanol-3-*β*-D-glucopyranoside (betuloside). Compound I was identified as an R configuration by a direct comparison of the $[\alpha]_D$ value with published data for R-rhododendrin.[4] Compound I had been obtained from the inner bark of *B. platyphylla*, *B. pendula*, and *B. pubescens* (Betulaceae).[3,4,7]

Compound II was positive in DSA, indicating that it was a phenolic compound. The M^+ of compound II was observed at m/z 328, and the acetyl derivative of compound II (IIA) gave the M^+ at m/z 496. The mass difference between the two molecular ions indicates the existence of four hy-

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Fig. 1. Structures of the glucosides of *p*-hydroxyphenyl derivatives isolated from the leaves of *Betula platyphylla* Sukatchev var. *japonica* Hara

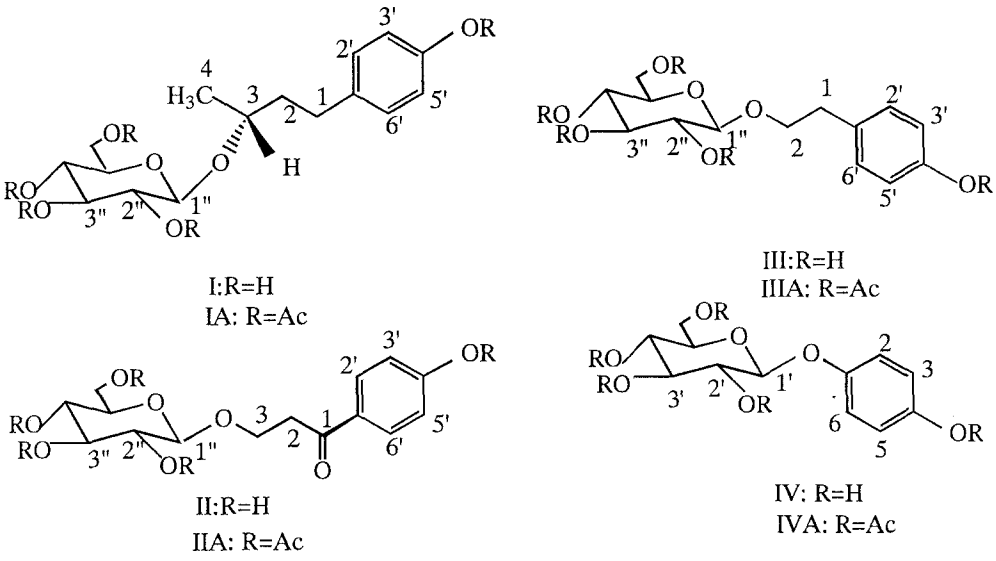

Table 1. ^{1}H-NMR spectral data of the acetates IA, IIA, IIIA, and IVA[a]

Protons	IA	IIA	IIIA	IVA
Aglycone moieties				
Aromatic rings				
H-2′, 6′ (H-2,6)*	7.19 (2H, d, J = 8.4 Hz)	7.87 (2H, d, J = 8.7 Hz)	7.20 (2H, d, J = 8.5 Hz)	7.00 (4H, s, H-2, 6/3, 5)
H-3′, 5′ (H-3,5)*	6.96 (2H, d, J = 8.4 Hz)	6.86 (2H, d, J = 8.7 Hz)	6.98 (2H, d, J = 8.5 Hz)	
Phenolic-OAc	2.27 (3H, s)		2.28 (3H, s)	2.29 (3H, s)
Side chains				
H-1	2.69 (2H, m)		2.88 (2H, m)	
H-2	1.84 (1H, m)	3.29 (1H, m)	3.64 (1H, m)	
	1.72 (1H, m)	3.06 (1H, m)	4.14 (1H, m)	
H-3	3.76 (1H, m)	4.04 (1H, m)		
		4.22 (1H, m)		
H-4	1.12 (3H, d, J = 6.4 Hz)			
Sugar moieties				
H-1″ (H-1′)*	4.50 (1H, d, J = 7.9 Hz)	4.58 (1H, d, J = 8.0 Hz)	4.47 (1H, m, J = 8.1 Hz)	5.03 (1H, d, J = 7.6 Hz)
H-2″ (H-2′)*	5.00 (1H, dd, J = 7.9, 9.8 Hz)	4.95 (1H, dd, J = 9.6, 8.0 Hz)	4.99 (1H, dd, J = 9.6, 8.1 Hz)	5.27 (2H, m, H-2′, 3′)
H-3″ (H-3′)*	5.21 (1H, t, J = 9.8 Hz)	5.20 (1H, t, J = 9.6 Hz)	5.18 (1H, t, J = 9.6 Hz)	
H-4″ (H-4′)*	5.11 (1H, t, J = 9.8 Hz)	5.07 (1H, t, J = 9.6 Hz)	5.08 (1H, t, J = 9.6 Hz)	5.16 (1H, m)
H-5″ (H-5′)*	3.66 (1H, m)	3.70 (1H, m)	3.68 (1H, m)	3.83 (1H, m)
H-6″ (H-6′)*	4.14 (1H, dd, J = 2.5, 12.3 Hz)	4.12 (1H, m)	4.11 (1H, m)	4.16 (1H, dd, J = 2.9, 12.8 Hz)
	4.24 (1H, dd, J = 4.4, 12.3 Hz)	4.26 (1H, m)	4.25 (1H, dd, J = 4.9, 12.3 Hz)	4.28 (1H, dd, J = 5.4, 12.1 Hz)
Alcoholic-OAc	2.01–2.05 (12H, m)	1.90–2.07 (12H, m)	1.91–2.09 (12H, m)	2.03–2.08 (12H, m)

s, singlet; d, doublet; dd, doublet doublet; m, multiplet; J, coupling constant; *, acetate IVA
[a] At 500 Hz, in CD_3OD, TMS as an internal standard

droxyl groups in compound II. An ^{1}H-NMR spectrum of the acetate IIA (Table 1) showed four singlets at δ 2.07, 2.02, 1.98, and 1.90, which were assigned to the methyl protons of four alcoholic acetoxy groups. However, no phenoxyl acetoxyl group was observed. The conflicting findings that compound II was positive in DSA and no phenolic acetoxyl group was observed in the ^{1}H-NMR spectrum of acetate IIA suggest that the phenolic hydroxyl group of compound II is resistant to the acetylation procedure. The AA'BB' type double doublet at δ 7.87 (2H, d, J = 8.7 Hz) and δ 6.86 (2H, d, J = 8.7 Hz) assignable to four aromatic protons of $C_{2',6'}$, $C_{3',5'}$ in the ^{1}H-NMR spectrum indicates the existence of a 1, 4-disubstituted benzene ring. The ^{13}C-NMR spectrum of acetate IIA revealed a signal from a carbonyl group at δ 196.3. The proton signals of $C_{2',6'}$ of acetate IIA (δ 7.87) in the ^{1}H-NMR spectrum, compared with those of acetate IA δ 7.19, shifted obviously downfield. The downfield shift was explained by the deshielding effect of the protons of $C_{2',6'}$ by the carbonyl group located at $C_{1'}$. This partial structure was supported further by the occurrence of a fragment ion at m/z 121 due to an (HO)ArC $\equiv$ O$^+$ moiety, also showing that a phenolic hydroxyl group is attached to $C_{4'}$. In the ^{1}H-^{1}HCOSY of acetate IIA, a correlation between two methylene protons C_2 [δ 3.06 (1H, m), 3.29 (1H, m)] and C_3 [δ 4.04 (1H, m), 4.22 (1H, m)] was observed.

The presence of a glucopyranosyl moiety in acetate IIA was clarified by comparing the ^{13}C-NMR spectrum (Table 2) with that of acetate IA. The mode of the glucosidic

Table 2. ^{13}C-NMR spectral data of the acetates IA, IIA, IIIA, IVA and compound I[a]

C	IA[b]	I[c]	IIA[b]	IIIA[b]	IVA[b]
Aglycone moieties					
Side chains					
C-1	30.7	33.3	196.3	35.3	—
C-2	38.5	42.0	38.1	70.5	—
C-3	74.7	76.6	65.9	—	—
C-4	19.9	19.9	—	—	—
Aromatic rings					
C-1′ (C-1)*	139.7	136.1	130.1	136.1	154.5
C-2′, 6′ (C-2, 6)*	129.5	131.9	130.9	130.0	122.6
C-3′, 5′ (C-3, 5)*	121.3	117.5	115.4	121.1	118.0
C-4′ (C-4)*	148.8	157.7	160.4	149.2	146.3
Sugar moieties					
C-1″ (C-1′)*	99.2	103.7	101.4	100.8	99.6
C-2″ (C-2′)*	71.6	76.6	71.3	71.1	71.2
C-3″ (C-3′)*	73.0	79.9	72.8	72.8	72.7
C-4″ (C-4′)*	68.6	73.2	68.4	68.4	68.3
C-5″ (C-5′)*	71.7	79.2	71.8	71.9	72.1
C-6″ (C-6′)*	62.1	64.3	61.9	61.9	62.0

[a] At 125 MHz, TMS as internal standard
[b] Measured in $CDCl_3$
[c] Measured in CD_3OD
*, Acetate IVA

linkage was determined to be β-form based on the coupling constant of the anomeric proton signal at δ 4.58 (1H, d, J = 8.0 Hz) in the ^{1}H-NMR spectrum of acetate IIA. The long-range connectivities observed in the HMBC spectrum of acetate IIa indicate that the anomeric proton signal at δ 4.58 correlates with the signal of C-3, showing that the location of the glucosyl residue is at the C-3 position. All these results support the idea that compound II is 3,4′-dihydroxypropiophenone-3-β-D-glucopyranoside, which had been obtained from the leaves of *B. alba*[8] and *B. platyphylla* var. *japonica*.[5]

Compound III was positive in DSA, indicating that it is a phenolic compound. The M^+ of compound III was observed at m/z 300, and the acetyl derivative of compound III (IIIA) gave an M^+ at m/z 510. The mass difference of the two molecular ions indicate that compound III had five free hydroxyl groups. An ^{1}H-NMR spectrum of the acetate IIIA (Table 1) showed the AA'BB' type double doublet at δ 7.20 (2H, d, J = 8.5 Hz) and 6.98 (2H, d, J = 8.5 Hz) assignable to four aromatic protons of $C_{2',6'}$ and $C_{3',5'}$, indicating the existence of a 1,4-disubstituted benzene ring. In the ^{1}H-^{1}HCOSY of acetate IIIA, a correlation between two methylene protons C_2 [δ 3.64 (1H, m), 4.14 (1H, m)] and C_1 [δ 2.88 (2H, m)] was observed. A singlet at δ 2.28 was assigned to the methyl protons of a phenolic acetoxyl group. The alcoholic acetoxyl groups gave four singlets at δ 2.09, 2.02, 1.96, and 1.91.

The presence of a glucopranosyl moiety in acetate IIIA was suggested by ^{13}C-NMR analysis (Table 2). The spectrum showed six resonances at δ 100.8 (C-1″), 72.8 (C-3″), 71.9 (C-5″), 71.1 (C-2″), 68.4 (C-4″), and 61.9 (C-6″), which were similar to those of acetate IA. The mode of the glucosidilic linkage was determined to be β-form based on the coupling constant of the anomeric proton signal at δ 4.47 (1H, d, J = 8.1 Hz) in the ^{1}H-NMR spectrum of acetate IIIA. The long-range connectivities observed in the HMBC spectrum revealed the connection between the glucosyl residue and aglycone. The anomeric proton signal at δ 4.47 was correlated with the signal of C-2, which shows that the glucosyl residue was linked to C-2.

Thus, it is conclued that compound III is 2-(4′-hydroxyphenyl) ethanol-2-β-D-glucopyranoside (salidroside), which had been obtained from the inner bark of *B. platyphylla* Sukatchev var. *japonica* Hara.[9]

Compound IV was obtained as an acetyl derivative IVA. The molecular ion peak (M^+) of the acetate IVA was observed at m/z 482. An ^{1}H-NMR spectrum of acetate IVA (Table 1) showed a singlet at δ 7.00 (4H) assignable to four aromatic protons that have the same environmental condition. A singlet at δ 2.29 was derived from the methyl protons of an acetoxyl group on the aromatic ring.

On the other hand, the existence of a glucopyranosyl moiety was suggested by ^{13}C-NMR analysis of acetate IVA (Table 2). The spectrum six resonances at δ 99.6 (C-1′), 71.2 (C-2′), 72.7 (C-3′), 68.3 (C-4′), 72.1 (C-5′), and 62.0 (C-6′) were assigned to those of a glucosyl residue by a comparision of the ^{13}C-NMR spectrum with those of acetate IA. The mode of the glucosidic linkage was determined to be β-form based on the coupling constant of the anomeric proton signal at δ 5.03 (1H, d, J = 7.6 Hz) in the ^{1}H-NMR spectrum of acetate IVA. Placement of the glucosyl residue on the aglycone was verified by use of the HMBC spectrum of acetate IVA. The anomeric proton signal at δ 5.03 correlated with the signal of the aromatic carbon of C-1. This result proves that the glucosyl residue was linked to C-1.

Thus, it is concluded that compound IV is 4-hydroxyphenyl-β-D-glucopyranoside (arbutin), which had been isolated from *Vaccinium vitisidea* L (Ericaceae)[10] and *Magnolia stellata* (Magnoliaceae).[11] The isolation of arbutin from shirakamba has not been reported so far.

We have isolated five glucosides of *p*-hydroquinone derivatives: 4-hydroxy-2-methoxyphenol-1-O-β-D-glucopyranoside (V), 4-hydroxy-3-methoxyphenol-1-O-β-D-glucopyranoside (VI), and 4-hydroxy-3-methoxyphenol-1-O-β-D-(6′-O-syringoyl) glucopyranoside (VII) from the inner bark of *Ostrya japonica* Sarg.; and 3,4-dimethoxy-5-hydroxyphenol-1-O-β-D-glucopyranoside (VIII) and 3,4,5-trimethoxyphenol-1-O-β-D-glucopyranoside (IX) from the sapwood of birch.[12,13] Confirmation of arbutin in birch leaves allowed us to report that all four types of the different *p*-hydroquinone glucosides correspond to the *p*-hydroxyphenyl type (P), guaiacyl type (G), G-5-OH, and syringyl type (S) pendant groups of phenylpropanoids in the wood of Betulaceae (Fig. 2).

Four glucosides of *p*-hydroxyphenyl derivatives have been found in many genera, and their formation may be a common phenomenon in plants (Table 3). However, the co-occurrence of C_6-C_4 (I), C_6-C_3 (II), C_6-C_2 (III), and C_6-C_0 (IV) structural compounds in shirakamba leaves is interesting from the viewpoint of their biogenetic relationship. These compounds may be precursors of arbutin, as all of them contained a *p*-hydroxyphenyl group, as discussed by Hayashi et al.[17]

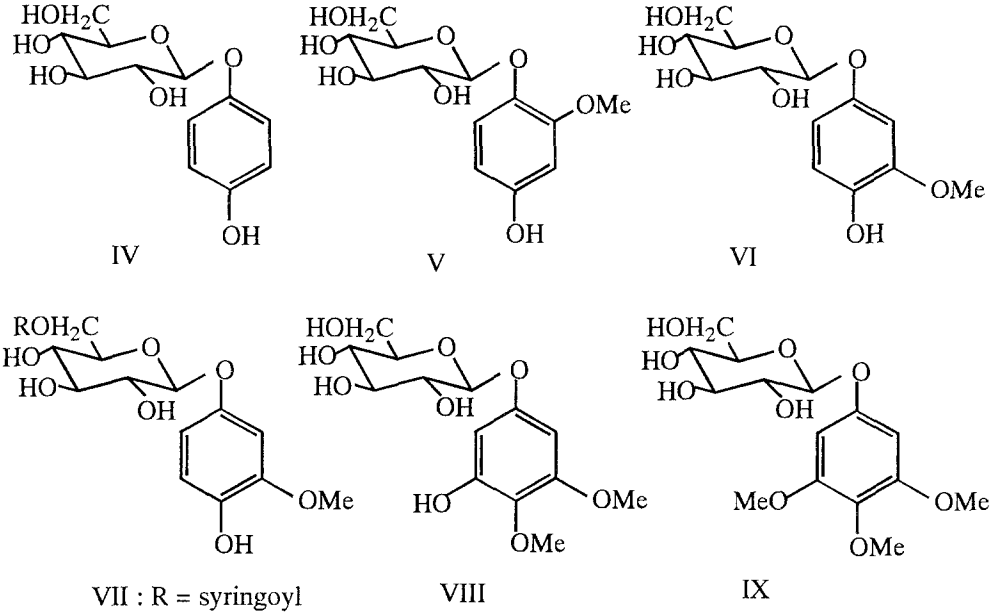

Fig. 2. P, G, G-5-OH, and S types of *p*-hydroquinone glucoside derivatives reported from the wood of Betulaceae

Table 3. Compounds I, II, III, and IV reported so far

Origin	Compound	References
Aceraceae		
Acer nikoense	I	14
Betulaceae		
Alnus glutinosa (shoot)	I	15
Betula platyphylla Sukatchev var. *japonica* Hara		
Inner bark	I, III	9, 16
Leaves	II	5
Betula alba		
Shoots	I	15
Leaves	II	8
Betula pendula (inner bark, twig)	I	3, 17
Betula pubescens (inner bark)	I	4
Ericaceae		
Vaccinium vitisidaea L.	IV	10
Oleaceae		
Fraxinus mandshurica Rupr var. *japonica* (inner bark)	III	9
Pinaceae		
Picea abies karst (root bark)	II	6
Magnoliaceae		
Magnolia stellata (leaves)	IV	11
Berberidaceae		
Epimedium diphyllum (aerial)	III	18

We have detected several other unknown compounds on thin-layer chromatography (TLC). Further research work on the extractives of the leaves of shirakamba is in progress, and the results will be reported in the near future.

Experiment

All spectroscopic and chromatographic methods in this work are the same as described in our previous paper.[1]

Isolation of compounds

Fractions were obtained from the ethanol (EtOH) extracts by extraction with EtOAc saturated with water. Each fraction was collected in 500-ml portions, monitored by TLC with (acetone:EtOAc:H_2O, 10:10:1, v/v) (AEAW). F_1–F_6 were obtained. F_3, F_4, and F_5 were rechromatographed on a silica gel column using CMW chloroform ($CHCl_3$):methanol:H_2O (CMW, 60:10:1, v/v). Each fraction was collected in 30-ml portions. F_{3-2} was combined, and compound I was crystallized from it. Recrystallization gave compound I (28.9 mg). F_{3-3} was combined and acetylated. The acetylation product was purifed by a preparative TLC with hexane: EtOAc (HEA, 1:1, v/v), and acetate IVA (2.0 mg) was obtained. Fractions of F_{4-1}–F_{4-8} were combined, and F_{4-8} was chromatographed on a silica gel column using CMW (60:10:1, v/v) as a developing solvent in 10-ml portions. F_{4-8-1}–F_{4-8-3} were combined. F_{4-8-1} was rechromatographed on a silica gel column using CMW (60:10:1, v/v) to yield compound III (3 mg). F_{5-1} was combined, and compound II was crystallized from it. During this recrystallization compound II (4.5 mg) was obtained.

Acetylations of the compounds were conducted with acetic anhydride and pyridine at 55°C for 24 h.

Compound I

Compound I was positive in DSA, Mp 188°–189°C, TLC (CMW, 40:10:1, v/v): Rf 0.30. FD-MS m/z: 328. Acetylation of compound I gave pentaacetate IA. TLC (HEA, 1:1, v/v): Rf 0.72. FD-MS m/z: 538 (M^+). $[\alpha]_D^{25}$ −28.8 (c = 0.13 in $CDCl_3$). UV λ_{max}^{EtOH}nm (log ε): 240 (3.16) and 289 (2.76). IR $\upsilon_{max}^{KBr}cm^{-1}$ (%): 2925 (72), 1751 (100), 1508 (38), 1375 (55), 1222 (77), 1039 (75), and 911 (29). EI-MS m/z: 496, 331, 169, 148, 107, and 43. ^{1}H-NMR($CDCl_3$): see Table 1. ^{13}C-NMR($CDCl_3$): see Table 2.

Compound II

Compound II was positive in DSA. Mp 158°–163°C, TLC (CMW, 40:10:1, v/v): Rf 0.2. FD-MS m/z: 328. Acetylation of the compound II gave tetraacetate IIA. TLC (HEA, 1:1, v/v): Rf 0.24. FD-MS m/z: 496 (M^+). $[\alpha]_D^{26}$ −19.9 (c = 0.41 in $CDCl_3$). UV $\lambda_{max}^{CHCl_3}$nm (log ε): 272.5 (4.10). IR $\upsilon_{max}^{KBr}cm^{-1}$ (%): 2959 (24), 1751 (100), 1604 (50), 1374 (45), 1225 (59), 1041 (73), and 757 (37). EI-MS m/z: 331, 148, 121, 93, and 43. ^{1}H-NMR($CDCl_3$): see Table 1. ^{13}C-NMR($CDCl_3$): see Table 2.

Compound III

Compound III was positive in DSA. TLC (CMW, 40:10:1, v/v): Rf 0.25. FD-MS m/z: 300 (M^+). Acetylation of compound III gave pentaacetate IIIA. TLC (HEA, 1:1, v/v): Rf 0.56. FD-MS m/z: 510 (M^+). $[\alpha]_D^{25}$ −9.24 (c = 0.24 in $CDCl_3$). UV λ_{max}^{EtOH}nm (log ε): 240 (3.89) and 270 (3.62). IR $\upsilon_{max}^{KBr}cm^{-1}$ (%): 2925 (74), 1751 (100), 1509 (30), 1370 (45), 1221 (57), 1041 (63), and 909 (26). ^{1}H-NMR ($CDCl_3$): see Table 1. ^{13}C-NMR($CDCl_3$): see Table 2.

Compound IV

Compound IV was positive in DSA. TLC (CMW, 40:10:1, v/v): Rf 0.12. Acetylation of compound IV gave pentaacetate IVA. TLC (HEA, 1:1, v/v): Rf 0.45. FD-MS m/z: 482 (M^+). $[\alpha]_D^{25}$ −7.99 (c = 0.24 in $CDCl_3$). UV $\lambda_{max}^{CHCl_3}$nm (log ε): 240 (3.22) and 282 (2.93). IR $\upsilon_{max}^{KBr}cm^{-1}$ (%): 2924 (69), 1756 (100), 1504 (52), 1371 (45), 1225 (74), 1046 (59), and 909 (27). EI-MS m/z: 331, 271, 229, 211, 169, 152, 127, 109, and 43. ^{1}H-NMR($CDCl_3$): see Table 1. ^{13}C-NMR($CDCl_3$): see Table 2.

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