EXPERIMENTAL

All the spectra were obtained on an MKh 1310 mass spectrometer using an IE24 source and LSIMS. Conditions for recording the EI spectra: SVP5 system for direct introduction, temperature of the ionization chamber and the evaporator bulb 200-180°C, ionizing voltage 70 V, collector current 60 μA, accelerating voltage 5 kV. For measuring the accurate masses of the ions the standard substance was perfluorokerosene, R ~ 10,000. Conditions for recording the LSIMS spectra: as the bombarding beam of primary ions we used Cs^+ with an energy of 7 keV, and accelerating voltage of 5 kV, and a temperature of the ionization chamber of 30-40°C. For the conditions used in obtaining the B/E spectra and the metastable defocussing spectra, see [2].

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TRITERPENE GLYCOSIDES OF Pulsatilla dahurica STRUCTURES OF GLYCOSIDES A, B, C, AND D

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The isolation of four triterpene glycosides from the roots of the dahurian anemone Pulsatilla dahurica (Fisch. ex DC) Spreng, is described together with their identification, on the basis of chemical transformations, spectral characteristics, and literature analogies, as hederagenin 3-O-α-L-arabinoside, hederagenin 3-O-[O-β-D-glucopyranosyl-(1→2)-α-L-arabinopyranoside], hederagenin 3-O-α-L-arabinopyranoside 28-O-[O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside], and hederagenin 3-O-[O-β-D-glucopyranosyl-(1→4)-α-L-arabinopyranoside] 28-O-[O-α-L-rhamnopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside].

Continuing a chemical study of the Far Eastern species of anemone [1], we have isolated a fraction of substances of glycosidic nature from the roots of the dahuriam anemone (Pulsatilla dahurica) (Fisch. ex DC Spreng), family Ranunculaceae. It was found to contain six compounds, which have been designated in order of increasing polarity as substances A, B, C, D, E, and F [2, 3]. In the present paper we discuss the establishment of the chemical structures of structures A (I), B (II), C (III), and D (IV).

The acid hydrolysis of compounds (I-IV) gave a common aglycon for them, which, by a comparison of physical constants, chromatographic mobilities, and ^{13}C NMR spectra with an authentic specimen, was identified as hederagenin (Table 1).

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TABLE 1. Chemical Shifts of the Signals of the ^{13}C Carbon Atoms of an Aglycon Moiety of Glycosides (I-IV), Progenins (VI)-(VII), and of Hederagenin (V) (pyridine, δ, ppm, 0 – TMS)

Atom C	I		III	IV	V	VI	VII
1	38,8	8	38,8	38,8	39,1	38,8	38,8
2	26,2	,2	26,0	26,0	27,8	26,1	26,0
3	82,2	82,4	82,2	82,3	74,0	82,0	81,9
4	43,5	43,5	43,4	43,3	43,5	43,3	43,3
5	47,8	48,0	47,8	47,7	49,2	47,6	47,5
6	18,5	18,4	18,3	18,3	18,9	18,2	18,0
7	33,1	33,2	33,0	33,0	33,4	32,9	33,0
8	40,0	39,8	40,0	39,9	40,1	39,8	39,6
9	48,3	48,1	48,2	48,1	48,4	48,1	47,9
10	37,1	37,0	37,0	36,9	37,5	36,9	36,8
11	24,0	23,9	23,7	23,7	24,0	23,7	23,6
12	122,4	122,4	122,2	122,7	122,7	122,4	122,3
13	144,7	144,7	144,0	143,9	144,9	144,6	144,6
14	42,4	42,3	42,2	42,1	42,5	42,1	42,5
15	28,5	28,5	28,3	28,2	28,6	28,3	28,2
16	24,0	23,8	23,5	23,5	24,0	23,7	23,6
17	46,8	46,7	47,1	47,0	46,9	46,6	46,4
18	42,2	42,1	41,7	41,7	42,3	41,9	41,9
19	46,6	46,5	46,3	46,3	46,8	46,4	46,4
20	31,0	30,9	30,7	30,7	31,1	30,9	30,8
21	34,5	34,3	34,1	34,0	34,5	34,2	34,2
22	33,4	33,2	32,6	32,5	33,3	33,2	33,1
23	64,8	64,7	64,8	64,9	68,7	64,5	64,4
24	13,6	13,4	13,5	13,4	13,2	13,6	13,4
25	16,2	16,2	16,2	16,1	16,2	16,1	15,9
26	17,7	17,5	17,6	17,7	17,4	17,3	17,3
27	26,4	25,9	26,0	25,8	26,4	26,1	26,0
28	179,8	179,8	176,3	176,2	180,0	180,1	180,1
29	33,4	33,2	33,0	33,0	33,4	33,2	33,1
30	24,0	23,9	23,7	23,5	24,0	23,7	23,6

The downfield shift of the C-3 signal of the aglycon in the ^{13}C NMR spectra of compounds (I)-(IV) (Table 1) relative to the signal in hederagenin (V) indicated the participation of the hydroxy group at C-3 in the formation of a glycosidic bond. In compounds (III) and (IV) the C-28 atom of the aglycon had also experienced a glycosylation effect. The latter conclusion was confirmed by the IR spectra of compounds (III) and (IV) (1740 cm^{-1}, ester group). Consequently, in each of compounds (III) and (IV) there was a carbohydrate unit attached to the carboxy group of the aglycon. This permitted compounds (I) and (II) to be assigned to the 3-O-monoglycosides, and compounds (III) and (IV) to the 3,28-O-bisglycosides of hederagenin.

The monosaccharides obtained on the acid hydrolysis of the glycosides under consideration were analyzed by TLC in the form of aldononitrile peracetates.

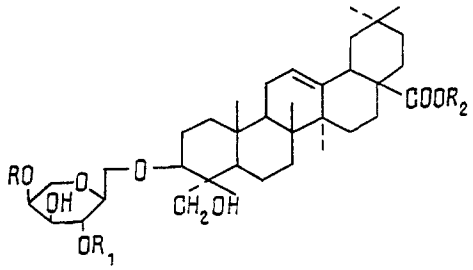
Arabinose was found as a component of glycoside (I). The ^{13}C NMR spectrum (Table 2) and the ^{1}H NMR spectrum of the carbohydrate moiety of glycoside (I) showed the signals of one anomeric carbon atom at 106.1 ppm and of one anomeric proton at 4.99 ppm. It followed from these facts that glycoside (I) was a hederagenin monoside. The SSCC $J_{1,2}$ = 7.33 Hz showed the α configuration of the anomeric center. Thus, glycoside (I) is described by formula (I) and is identical with leontoside [4] (see top of following page).

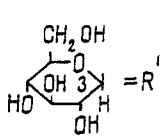
According to GLC results, the carbohydrate component of glycoside (II) consisted of arabinose and glucose residues (1:1). This was confirmed by the ^{13}C NMR spectrum (Table 2) and the ^{1}H NMR spectrum, which showed the signals of two anomeric carbon atoms at 103.6 and 105.6 ppm and the signals of two anomeric protons at 5.19 and 5.18 ppm. The values $J_{1,2}$ = 7.0 and 7.8 Hz showed the α- and β-configurations of the anomeric centers of the arabinopyranosyl and glucopyranosyl residues, respectively.

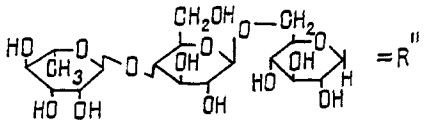
The assignment of the signals with the use of partially relaxed spectra permitted the identification of the signals of the terminal monosaccharide, which coincided with those of a β-D-glucopyranoside [5]. With respect to the values of the chemical shifts, the remaining signals coincided with those of a 2-O-substituted α-L-arabinopyranoside [6]. On the basis of the facts given, glycoside (II) was shown to be identical with glycoside B isolated previously from Caulophyllum robustum [7] and consisting of hederagenin 3-O-[O-β-D-glucopyranosyl(1→2)-α-L-arabinopyranoside] (formula II).

TABLE 2. Chemical Shifts of the Signals of the ^{13}C Carbon Atoms of the Carbohydrate Moieties of Glycosides (I-IV) and of Progenins (VI) and (VII) (pyridine, δ, ppm, 0 – TMS)

C atom	I	II	III	IV	VI	VII
Ara_p						
1	106,1	103,6	106,1	105,9	106,4	106,2
2	73,0	81.1	73,0	73,4	73,0	73,4
3	74,5	73,4	74,5	74,4	74,6	74,4
4	69,3	68,1	69,3	79,3	69,4	79,6
5	66,5	66,2	66,5	66,0	66,8	66,1
$Glc_{p(3)}$						
1		105,6		106,3		106.6
2		76,0		75,5		75,5
3		78,2		78,4		78,4
4		71,5		71,3		71,1
5		78,2		78,1		78,1
6		62,6		62,6		62,3
Rha_p						
1			102,6	102,5		
2			72,6	72,6		
3			72,3	72,2		
4			73,8	73,7		
5			70,2	70,2		
6			18,3	18,3		
$Glc_{p(2)}$						
1			104,6	104,5		
2			75,1	75,0		
3			76,5	76,4		
4			78,6	78,3		
5			76,9	76,8		
6			61,5	61.4		
$Glc_{p(1)}$						
1			95,5	95,4		
2			73,8	73,7		
3			78,7	78,6		
4			71,0	70 8		
5			77,8	77,7		
6			69,3	69,9		







I. R=H; R_1=H; R_2=H
II. R=H; R_1=R'; R_2=H
III. R=H; R_1=H; R_2=R''
IV. R=R'; R_1=H; R_2=R''
VI. R=H; R_1=H; R_2=H
VII. R=R'; R_1=H; R_2=H

According to GLC results, glycoside (III) was hederagenin tetraoside. Its carbohydrate component consisted of arabinose, rhamnose, and glucose (1:1:2). This was also shown by the ^{13}C NMR spectrum of glycoside (III) (Table 2) in which the signals of four anomeric protons were detected at 106.1, 104.6, 102.6, and 95.5 ppm.

TABLE 3. ^{13}C NMR Spectrum of the Oligosaccharide from Glycosides (III) and (IV) (D_2O, δ_{MeOH} = 49.6 ppm, 40°C)

C atom	Glc_p (1) α-form	Glc_p (1) β-form	Glc_p (2)	Rha_p
1	92,8	96,7	103,2	101,4
2	72,2	74,8	74,1	70,9
3	73,4	76,4	75,1	71,1
4	70,3	70,3	78,2	72,6
5	70,9	75,5	75,7	69,8
6	69,5	69,5	61,1	17,2

Alkaline hydrolysis of the ester glycosidic bond of glycoside (III) gave an oligosaccharide and progenin (VI) [formula (VI)], which were identical with glycoside (I), i.e., hederagenin 3-O-α-L-arabinopyranoside.

Analysis of the ^{13}C NMR spectrum of the oligosaccharide (Table 3) showed that it consisted of an anomeric mixture of O-α-L-rhamnopyranosyl-(1→4)-O-β-D-glucopyranosyl-(1→6)-(α- and β-)D-glucopyranoses. Thus, the signals of the anomeric carbon atoms (chemical shifts 92.8 and 96.7 ppm) at the reducing end of the oligosaccharide corresponded to those of α- and β-D-glucopyranose residues [8]. The spectrum of the oligosaccharide lacked signals corresponding to a terminal D-glucopyranose. On the basis of these facts it was possible to state that the terminal monosaccharide residue could only be rhamnopyranose.

The downfield chemical shift of the carbon atom of the substituted hydroxymethyl group (69.5 ppm) its ready splitting because of anomerization in comparison with the signals of the carbon atom of a free hydroxymethyl group (61.1 ppm), and the strict singlet nature of the latter in the spectrum with complete decoupling from protons permitted the statement that the D-glucopyranose residue present at the reducing end of the oligosaccharide was linked by a 1→6 bond. Furthermore, the α-effects from the addition of β-glucose and α-rhamnose residues to the C-6 atom of glucose are different, and in the second case for the substituted C-6 of glucose we would have chemical shifts lower by 1-2 ppm [9].

The internal β-D-glucopyranosyl residue (signal of its anomeric carbon atom 103.2 ppm) could be substituted only at C-4 according to the chemical shift of this signal (78.2 ppm) and also to the absence of a signal of a chemical shift in the region of 77.1 ppm which would be characteristic for C-2 in the case of substitution at C-2 of a glucopyranose. A comparison of the spectra of the oligosaccharide moiety of glycoside (III) (Table 3) with literature figures [10] led to similar conclusions.

Summarizing the results obtained and comparing them with literature figures for glycosides of established structure [11, 12], we were justified in concluding that the (III) was identical with cauloside D [13] and was hederagenin 3-O-α-L-arabinopyranoside 28-O-[O-L-rhamnopyranosyl(1→4)-O-β-D-glucopyranoside-(1→6)-β-D-glucopyranoside] [formula (III)]. According to GLC results, glycoside (IV) was a hederagenin pentaoside. A confirmation of this was the five signals in the weak-field region of the ^{13}C NMR spectrum of glycoside (IV) with chemical shifts of 105.9, 106.3, 95.4, 104.5, and 102.5 ppm (Table 2), belonging to the anomeric carbon atoms of sugar residues.

The alkaline hydrolysis of glycoside (IV) gave an oligosaccharide identical with the oligosaccharide obtained on the alkaline hydrolysis of glycoside (III), together with progenin (VII) [formula (VII)].

According to GLC results, the carbohydrate component of progenin (VII) contained arabinose and glucose residues (1:1). In the weak-field region of the ^{13}C NMR spectrum (Table 2) and the ^1H NMR spectrum of progenin (VII) we detected the signals of two anomeric carbon atoms, at 106.2 and 106.6 ppm, and the signals of two anomeric protons, at 5.23 ppm with $J_{1,2}$ = 7.63 Hz and at 4.93 ppm with $J_{1,2}$ = 7.33 Hz. The latter values corresponded to the protons at the anomeric carbon of an α-arabinopyranosyl residue (according to the ^1H NMR spectrum of hederagenin 3-O-α-L-arabinopyranoside described above), while the signal at 5.23 ppm related to the protons at the anomeric carbon atom of a glucopyranosyl residue. The $J_{1,2}$ value of 7.63 Hz showed the β-configuration at the anomeric center of this sugar residue.

The H-2 and H-3 protons of the arabinopyranosyl residue resonated at 4.40 and 4.10 ppm, respectively (the assignment of the signals was made with the use of the double-resonance procedure). In the NMR spectrum of the ^{13}C NMR atoms selectively decoupled from the H-2 and H-3 protons, the C-2 and C-3 atoms of the arabinopyranosyl residue resonated at 74.4 and 73.4 ppm, respectively. This permitted the assumption that the C-2 and C-3 carbon atoms of the arabinopyranosyl residue did not participate in the formation of glycosidic bonds, since otherwise one of them should have resonated in a relatively weak field (76-85 ppm). Consequently, the arabinopyranosyl residue was substituted at the C-4 carbon atom.

The Hakomori methylation of progenin (VII) followed by methanolysis and acetylation led to the identification (by GLC), of methyl 4-O-acetyl-2,3-di-O-methyl-α-L-arabinopyranoside [14] and methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside [15], which definitively confirmed the presence of the glycosidic bond at the C-4 carbon atom of the arabinopyranosyl residue. Thus, progenin (VII) was hederagenin 3-O-[O-β-D-glucopyranosyl-(1→4)-α-L-arabinopyranoside] and was identical with leontoside B [4]. Consequently, glycoside (IV) was hederagenin 3-O-[O-β-D-glucopyranosyl(1→4)-α-L-arabinopyranoside 28-O-[O-α-L-rhamnopyranosyl-(1-4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranoside], identical with leontoside D [16] and is described by formula (IV).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were taken on a Bruker WM-250 Fourier spectrometer with a working frequency of 250 MHz for ^{1}H and 62.9 MHz for ^{13}C at 40°C, and IR spectra were obtained on a Specord 75 IR spectrometer in KBr. Optical rotations were measured on a Perkin-Elmer 141 instrument in a cell with ℓ = 10 cm at 20°C, and melting points on a Boëtius stage. Mass spectra were obtained on an LKB-9000 S instrument at an ionizing energy of 70 eV. TLC was conducted on a Tsvet 101 chromatograph. The monosaccharides, in the form of partially methylated acetates of methylglycosides, were chromatographed on columns (3 mm × 2.5 m) containing Inerton AW-DMCS impregnated with the liquid phase QF-1 (2%) with programming of the temperature from 125 to 225°C at the rate of 5°C/min, the carrier gas being helium at a rate of flow of 60 ml/min. The aldononitrile peracetate derivatives of the sugars were chromatographed under the same conditions. For quantitative determinations we used mannose as internal standard. The sugars were identified from their T_{rel} values in comparison with authentic samples.

HPLC was conducted on a GSP-100 instrument (Czechoslovakia) using steel columns (3.3 × 150 mm) filled with the reversed-phase sorbent Separon SGX C_{18} (7 μm). The space velocity of the eluent system (water) was 1 ml/min. The components were detected by means of a differential refractometer.

Thin-layer chromatography (TLC) was conducted on Silufol, Silicagel 60 (Merck), and silica gel KSK (5 μm) plates fixed with a silicic acid sol [17]. The substances were detected by spraying the plates with 10% sulfuric acid in ethanol following by heating at 100-150°C for 5-10 min. Column chromatography was performed on silica gels KSK and L (63-100 μm) and on Fractogel TSK-HW-40 (Japan). The following solvent systems were used: 1) chloroform–methanol [a) (2:1), b) (40:1) → (40:35), c) (20:1) → (20:6), d) (10:1) → (2:1)]; 2) chloroform–methanol (40:1) → (1:2); 3) benzene–acetone (10:1) → (2:1); 4) n-butanol–ethanol–20% ammonia solution (10:2:5); 5) hexane–acetone (2:1); 6) n-butanol–ethanol–water (5:5:3); 7) hexane–ethyl acetate (1:1).

Isolation of the Glycoside. The air-dry comminuted roots of dahurian anemone (1.2 kg) gathered in the period at the end of flowering–beginning of fruit-bearing were treated three times with chloroform and were exhaustively extracted with 80% ethanol at room temperature. The concentrated extract obtained after the ethanol had been distilled off was diluted with water in a ratio of 1:1 and was repeatedly reextracted with n-butanol. The butanolic extracts were combined and washed with water, and the dry residue obtained after the solvent had been distilled off was dissolved in a small amount of methanol. This solution was poured into acetone and the resulting precipitate was filtered off, washed with cold acetone, and dried. This gave 66.4 g (5.53%; here and below the yields are calculated on the air-dry raw material) of a total glycosidic fraction, in which six substances were detected which were designated in order of increasing polarity as A, B, C, D, E, and F (GLC, silica gel, system 4). Part of this fraction (20 g) was chromatographed on silica gel L (400 g) using system 2. This yielded four fractions enriched with substances A, B, C, and D. Then each fraction was rechromatographed on silica gel KSK. Elution with system 3 gave glycoside (I)

in an amount of 0.11 g (0.03%); system 1b gave 0.39 g (0.11%) of glycoside (II); system 1c gave 0.54 g (0.15%) of glycoside C, and system 1d gave 2.20 g (0.61%) of glycoside (IV).

Substance A (I). $C_{35}H_{56}O_8$, mp 224-228°C (from methanol), $[\alpha]_D^{20}$ +44.2° (c 0.55; dimethyl sulfoxide); IR spectrum (ν, cm^{-1}): 3414 (OH), 1696 (C=O of a carboxy group). The ^1H spectrum of the carbohydrate moiety of glycoside A had the following proton signals (δ, ppm): 4.99 (H-1, $J_{1,2}$ = 7.33 Hz); 4.44 (H-2, $J_{2,1}$ = 7.33 Hz, $J_{2,3}$ = 9.16 Hz); 4.07 (H-3, $J_{3,2}$ = 9.16 Hz, $J_{3,4}$ = 3.16 Hz); 4.26 (H-4, multiplet); 3.72 (H-5a, $J_{5a,5e}$ = 10.69 Hz, $J_{5a,4}$ = 3.67 Hz); 4.31 (H-5e, multiplet).

Substance B (II). $C_{41}H_{66}O_{13}$, mp 248-251°C, $[\alpha]_D^{20}$ +38.7° (c 0.56; dimethyl sulfoxide); IR spectrum (ν, cm^{-1}): 3406 (OH), 1690 (C=O of a carboxy group).

Substance C (III). $C_{53}H_{88}O_{25}$, mp 205-209° (decomp.), $[\alpha]_D^{20}$ +4.8° (c 0.51; dimethyl sulfoxide); IR spectrum (ν, cm^{-1}): 3416 (OH), 1740 (ester group).

Substance D (IV). $C_{59}H_{98}O_{30}$, mp 208-215°C (decomp.), $[\alpha]_D^{20}$ +0.9° (c 0.52; dimethyl sulfoxide); IR spectrum (ν, cm^{-1}): 3400 (OH), 1740 (ester group).

Acid Hydrolysis of Glycosides (I-IV). Glycosides (I-IV) (20 mg each) were hydrolyzed with 5% hydrochloric acid (4 ml) for 4 h. After cooling, in each case, 2 ml of water was added and the water-insoluble products were extracted with diethyl ether (3 × 4 ml). The ethereal extracts were combined and were washed with water, and the solvent was driven off. In the dry residues of glycoside (I)-(IV) a common aglycon – hederagenin – was identified by comparison with an authentic sample (TLC, Silufol, system 5). The aqueous part of the hydrolysate was evaporated to dryness. The monosaccharides obtained on the hydrolysis of glycosides (I-IV) were analyzed in the form of aldononitrile peracetates, which were obtained by a known procedure [18, 19]. By GLC and comparison with authentic samples, arabinose was identified for glycoside (I), arabinose and glucose (1:1) for (II), and arabinose, rhamnose, and glucose in ratios of 1:1:2 and 1:1:3, respectively, for (III) and (IV).

Alkaline Hydrolysis of Glycosides (III) and (IV). Glycosides (III) (80 mg) and (IV) (210 mg) were hydrolyzed with a 3% solution of KOH (10 and 50 ml, respectively) at room temperature for 4 h. The hydrolysates were neutralized with KU-2 cation-exchange resin in the H^+ form to pH 5-6, and the resin was filtered off. The aqueous solution was extracted with n-butanol, the solvent was evaporated to dryness, and the residue was chromatographed on silica gel KSK. By elution with system 3, glycoside (III) yielded 31 mg of progenin (VI), $C_{35}H_{56}O_8$, mp 225-230°C, $[\alpha]_D^{20}$ +44.0° (c 0.40; dimethyl sulfoxide). IR spectrum (ν, cm^{-1}): 3460 (OH), 1700 (C=O of a carboxy group). By elution with system 1b, glycoside (IV) yielded 78 mg of progenin (VII), $C_{41}H_{66}O_{13}$, mp 238-245°C, $[\alpha]_D^{20}$ +4.08° (c 0.56; dimethyl sulfoxide). IR spectrum (ν, cm^{-1}): 3440 (OH), 1696 (C=O) of a carboxy group. Progenins (VI) and (VII) were hydrolyzed with 5% hydrochloric acid as described above. The following sugars were identified in the form of aldononitrile peracetates by the GLC method: arabinose for progenin (VI), and arabinose and glucose in a ratio of 1:1 for progenin (VII).

The alkaline hydrolysate after treatment with butanol was evaporated to dryness, and the residue was chromatographed on a column filled with Fractogel TSK-HW-40, which was eluted with water. The oligosaccharides were purified finally by the HPLC method. The purity of the products was checked by TLC on Silicagel 60 plates (Merck), system 6. Glycosides (III) and (IV) yielded 15 and 35 mg of oligosaccharide, respectively.

Permethylate of Progenin (VII). Progenin (VII) (58 mg) was methylated by Hakomori's method [20]. After extraction with chloroform, the methylation products were purified on silica gel KSK, using system 7. The chromatographically homogeneous product (TLC, Silicagel KSK, system 7) was treated in sealed tube with 2 ml of absolute methanol containing 0.2 ml of acetyl chloride at 100°C for 3 h. The methyl esters of methyl glycosides obtained were acetylated (pyridine–acetic anhydride (1:1), room temperature for 12 h) and the acetates were analyzed by GLC–MS. The following were identified by analogy with literature figures [14, 15]: methyl 4-O-acetyl-2,3-di-O-methyl-α-L-arabinopyranoside, m/z (%) 204(0.08), 203(0.08), 116(1.35), 101(46.00), 88(100.00), 87(2.70), 75(35.00), 74(2.70), 45(35.14), 43(9.46), and methyl 2,3,4,6-tetra-O-methyl-β-D-glucopyranoside, m/z (%) 219(0.20), 187(1.10), 176(1.82), 149(4.54), 127(1.82), 101(43.64), 88(100.00), 75(50.01), 73(14.55).

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