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Two New Triterpenoid Saponins from the Seeds of *Aesculus chinensis*

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Abstract: Two new triterpenoid saponins, named isoescins IIIa (**1**) and IIIb (**2**) were isolated from the seeds of *Aesculus chinensis* and identified by spectroscopic analysis and chemical hydrolysis. Their structures were established as 21β-tigloyl-28-acetylbarringtogenol C-3β-O-[β-D-galactopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)]-β-D-glucopyranosiduronic acid (**1**) and 21β-angeloyl-28-acetylbarringtogenol C-3β-O-[β-D-galactopyranosyl (1→2)] [β-D-glucopyrano-syl (1→4)]-β-D-glucopyranosiduronic acid (**2**), which are geometrically isomeric.

Keywords: *Aesculus chinensis*, isoescins IIIa and IIIb.

Aesculus chinensis Bge. (Hippocastanaceae) is a native plant to China. Escins, the saponin mixtures from the seeds, have shown prominent anti-inflammatory activity and are of great medicinal importance. Recently, detailed chemical work has been undertaken on escins and more than ten saponins have been isolated and identified by spectroscopic techniques[1-5]. Repeated chromatography of escins afforded two new triterpenoid oligoglycosides, named isoescins IIIa (**1**) and IIIb (**2**). The present paper describes the structural elucidation of them.

Compound **1** was isolated as an amorphous powder. The IR spectrum displayed absorption peaks at 1710 and 1598 cm^{-1} for the carbonyl group and the α, β-unsaturated ester and broad bands at 3409 and 1042cm^{-1} for the oligoglycosidic structure. The MALDI-TOF-MS showed the molecular ion peak at *m/z* 1137 $[M+Na]^+$, corresponding to the molecular composition of $C_{55}H_{86}O_{23}$, identical with escin IIIa[4]. The ion peak at *m/z* 814 implied the loss of two hexoses.

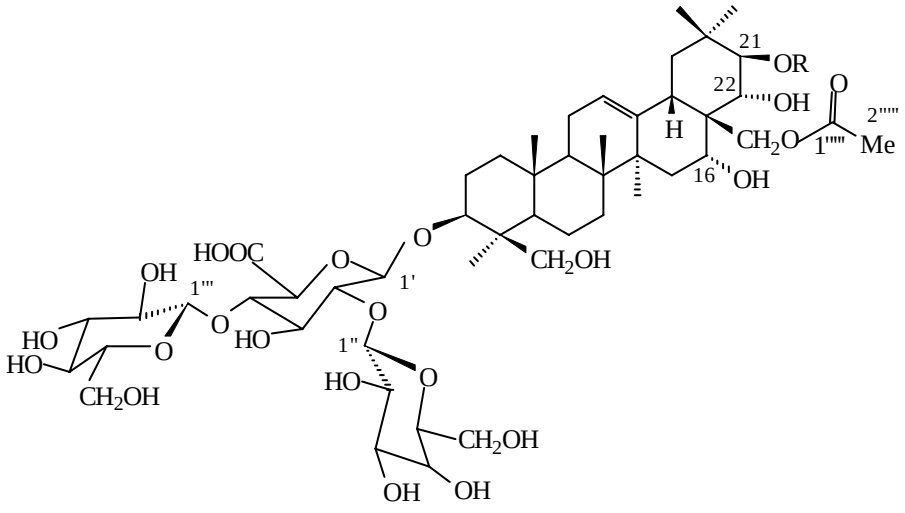
The ^1H and ^{13}C NMR signals were assigned by the combination of HMQC and HMBC spectra. In addition to ^1H and ^{13}C NMR signals due to a tigloyl group [^1H NMR: δ7.00 (H-3""), 1.83 (Me-5"") and 1.57 (Me-4""); ^{13}C NMR: δ168.4 (C-1""), 129.8 (C-2""), 136.2 (C-3""), 14.1 (C-4"") and 12.4 (C-5"")] and an acetyl group [^1H NMR: δ2.00 (Me-2""""); ^{13}C NMR: δ170.7 (C-1"""") and 20.7 (C-2"""")], signals ascribable to a pentacyclic triterpenoid sapogenol were observed. Those at δ123.3 (C-12) and 142.7 (C-13) with the corresponding proton at δ5.48 (br s, H-12) were indicative of a double bond at the 12-position of an oleanane skeleton. Compared with the NMR data of isoescin IIa[5], however, the carbon signal of 24-CH_2OH disappeared and the signals of the neighboring carbons also shifted. An additional methyl group was observed at δ16.7

(Me-24) in the ^{13}C NMR and δ1.04 (Me-24) in the ^{1}H NMR. Therefore, compound **1** must have a skeleton of barringtogenol C. The chemical shifts for rings D and E of the aglycone were found to be coincident with those of isoescin IIa, which suggested that it may have the same substitution patterns for the two acyl groups. In the HMBC spectrum, the correlation peak between the carbonyl carbon of the tigloyl group (δ168.4) and H-21 (δ6.45, d, *J*=9.5Hz) also confirmed the structure.

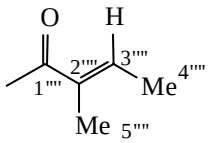
Three monosaccharide residues in the structure were evident from anomeric carbon signals at δ104.8 (C-1'), 105.1 (C-1") and 104.4 (C-1'") together with corresponding protons at δ4.75 (H-1', d, *J*=7.5Hz), 5.31 (H-1", d, *J*=6.5Hz) and 5.30 (H-1'", d, *J*=7.5Hz). Acid hydrolysis of **1** yielded glucuronic acid, glucose and galactose. The chemical shifts for the sugar moiety resembled those of escin IIIa[4], which suggested the same trisaccharide moiety as escin IIIa.

Consequently, the structure of **1** was identified as 21β-tigloyl-28-acetylbarring-togenol C-3β-O-[β-D-galactopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)]-β-D-gluco-pyranosiduronic acid, and named isoescin IIIa.

Scheme 1 The Structures of Compounds **1** and **2**



1 R=Tig =



2 R=Ang =

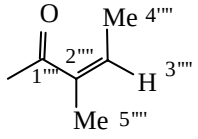


Table ^{13}C NMR Spectral Data of Compounds **1** and **2** (δ Relative to TMS in pyridine-d_5, 125MHz)

C	1	2	C	1	2
1	38.7	38.7	1'	104.8	104.8
2	26.4	26.4	2'	82.9	82.3
3	89.4	89.3	3'	76.3	76.8
4	39.4	39.4	4'	81.5	81.1
5	55.6	55.6	5'	75.0	74.9
6	18.3	18.3	6'	175.5	173.3
7	33.0	33.0	1''	105.1	105.2
8	40.0	39.9	2''	74.9	74.9
9	46.9	46.9	3''	75.0	74.9
10	36.7	36.6	4''	71.1	71.0
11	23.9	23.8	5''	76.8	76.8
12	123.3	123.0	6''	62.1	62.0
13	142.7	142.7	1'''	104.4	104.5
14	41.7	41.7	2'''	74.9	74.9
15	34.6	34.6	3'''	78.1	78.1
16	67.6	67.6	4'''	71.3	71.3
17	47.0	47.0	5'''	78.1	77.8
18	40.5	40.5	6'''	62.8	62.8
19	47.2	47.2	1''''	168.4	168.5
20	36.3	36.0	2''''	129.8	129.4
21	79.7	79.7	3''''	136.2	135.7
22	71.7	71.7	4''''	14.1	15.8
23	28.0	27.9	5''''	12.4	20.9
24	16.7	16.7	1'''''	170.7	170.6
25	15.6	15.6	2'''''	20.7	20.6
26	17.0	16.9			
27	27.4	27.4			
28	66.4	66.4			
29	29.7	29.7			
30	20.1	20.2			

Compound **2** was also obtained as an amorphous powder. The IR spectrum showed absorption bands at 3406 and 1074cm^{-1} for the oligoglycosidic structure along with those at 1711 and 1600cm^{-1} for the α, β-unsaturated ester and the carboxyl group. The MALDI-TOF-MS showed quasimolecular ion peak at *m/z* 1137 $[M+Na]^+$, identical with **1**. The fragmental ion peak generated by the elimination of two hexoses was also observed at *m/z* 814.

The NMR data further characterized the structure of the saponin. The ^1H and ^{13}C chemical shifts of **1** and **2** were so much alike, both including signals belonging to the barringtogenol C skeleton[4, 6, 7] [seven quaternary methyl groups at δ0.80 (Me-25), 0.96 (Me-26), 1.03 (Me-24), 1.09 (Me-29), 1.16 (Me-23), 1.28 (Me-30) and 1.81 (Me-27) in the ^1H NMR], a trisaccharide moiety [^1H NMR: δ4.79 (d, *J*=7.5Hz, H-1'), 5.32 (d, *J*=7.5Hz, H-1''') and 5.33 (d, *J*=6.5Hz, H-1''); ^{13}C NMR: δ104.8 (C-1'), 105.2 (C-1'') and 104.5 (C-1''')] and an acetyl group [^1H NMR: δ1.94 (Me-2''''); ^{13}C NMR: δ170.6 (C-1'''') and 20.6 (C-2'''')]. The only difference between them was diagnostic signals of an angeloyl group. Instead, carbon signals at δ168.5 (C-1''''), 129.4 (C-2''''),

135.7 (C-3""), 15.8 (C-4"") and 20.9 (C-5"") and proton signals at δ1.94 (Me-5""), 2.01 (Me-4"") and 5.87 (H-3"") were observed indicating the replacement by an angeloyl group. Furthermore, glucuronic acid, glucose and galactose were also detected by PC after mild acid hydrolysis of **2**.

Consequently, **2** was identified as 21β-angeloyl-28-acetylbarringtogenolc 3β-O-[β-D-galactopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)]-β-D-glucopyranosiduronic acid, and named isoescin IIIb. It is a geometrical isomer of **1**.

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