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

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Abstract: Three new triterpenoid saponins, escins IVc (**1**), IVd (**2**) and IVf (**3**) were isolated from the seeds of *Aesculus chinensis*. They were determined as 22α-tigloyl-28-acetylprotoaescigenin-3β-O- [β-D-glucopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)]-β-D-glucopyranosiduronic acid **1**, 22α-angeloyl-28-acetylprotoaescigenin-3β-O-[β-D-glucopyranosyl (1→2)] [β-D-glucopyrano- syl (1→4)]-β-D-glucopyranosiduronic acid **2** and 28-tigloyl protoaescigenin-3β-O- [β-D-gluco-pyranosyl (12)] [β-D-glucopyranosyl (1→4)] -β-D-glucopyranosiduronic acid **3**.

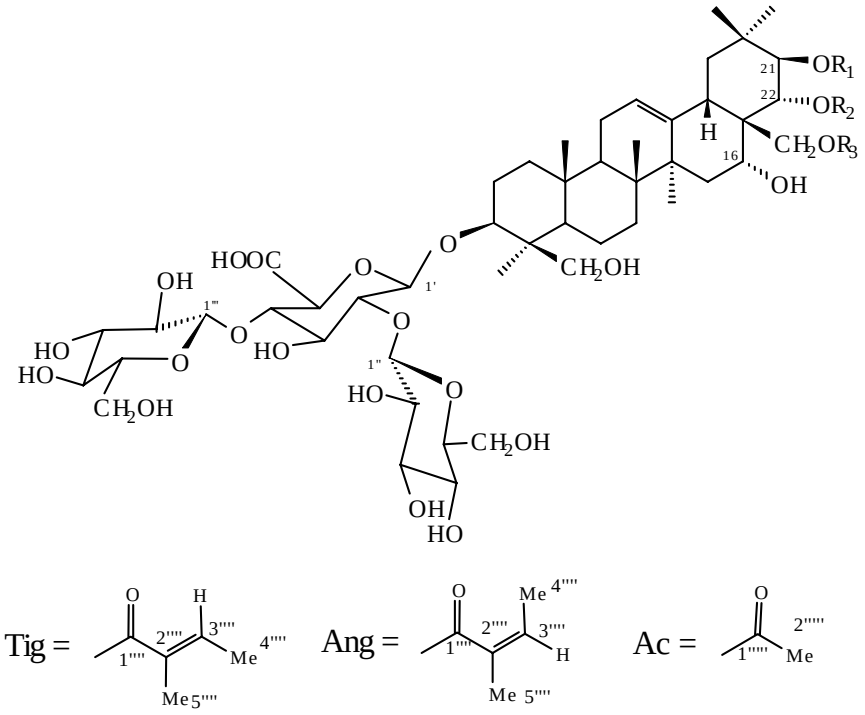
Keywords: Triterpenoid saponins, *Aesculus chinensis*, escins IVc, IVd and IVf.

In previous papers we have reported the isolation and identification of escins Ia, Ib, IVa, IVb and IVe[1, 2]. Now we describe the structure elucidation of three more new triterpenoid saponins, named escins IVc (**1**), IVd (**2**) and IVf (**3**).

Compound **1** was isolated as white amorphous powder. HR-SI-MS revealed the composition of $C_{55}H_{86}O_{24}$ by molecular ion peak at *m/z* 1129.5438. Compared with the ^{13}C and ^{1}H NMR spectra of escin Ia, compound **1** is also a glycoside of protoaescigenin acylated by the tigloyl and the acetyl group. The significant differences between them were the chemical shifts of C-21 (δ76.2) and C-22 (δ77.9) with the corresponding protons at δ4.95 and 5.92. In addition, minor changes were also observed for C-17 (δ45.9), C-18 (δ41.4) and H-18 (δ2.75). The stereochemistry of C-21 and C-22 remained unchanged as demonstrated by NOESY spectrum: Me-29 showed a strong NOE correlation with H-21 while Me-30 correlated with H-22 strongly. This was consistent with escin Ia. The attachments of the tigloyl group at C-22 and the acetyl group at C-28 were derived from HMBC experiment, which correlated the carbonyl carbons of the tigloyl and the acetyl group to H-22 (δ5.92) and H-28 (δ4.02) respectively. In addition, the number of monosaccharides in the structure was suggested by three anomeric carbon resonances at δ104.4, 104.0 and 104.4 with the corresponding anomeric protons at δ4.87, 5.58 and 5.18. ^{1}H and ^{13}C NMR signals of the trisaccharide moiety were coincident with those of escin Ia[1, 3]. And acid hydrolysis of compound **1** also yielded glucose and glucuronic acid. Their sequences and linkage sites were further confirmed by HMBC correlations between the following pairs: C-3 (δ90.9) and H-1' (δ4.87); C-2' (δ79.5) and H-1" (δ5.58); and C-4' (δ81.7) and H-1'" (δ5.18). Hence,

compound **1** was established as 22α-tigloyl-28-acetylprotoaescigenin-3β-O-[β-D-glucopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)] -β-D-glucopyranosiduronic acid, and named escin IVc.

Figure 1. Structures of Compounds **1~3**



	R_1	R_2	R_3
1	H	Tig	Ac
2	H	Ang	Ac
3	H	H	Ang

Compound **2** was determined to be an isomer of **1**. HRMALDI MS showed the quasimolecular ion peak at *m/z* 1153.5406 $[M+Na]^+$, consistent with the molecular formula of $C_{55}H_{86}O_{24}$. The only differences between them in ^1H and ^{13}C NMR spectra were signals due to an angeloyl group [^{13}C NMR: δ168.1 (C-1""), 129.1 (C-2""), 136.6 (C-3""), 15.7 (C-4"") and 20.6 (C-5""); ^1H NMR: δ5.83 (H-3""), 1.43 (Me-4"") and 1.92 (Me-5"")] replaced those due to a tigloyl group. Similar HMBC and NOE correlations were also present for **2**. Therefore, compound **2** was identified as 22α-angeloyl-28-acetyl-protoaescigenin-3β-O- [β-D-glucopyranosyl (1→2)] [β-D-gluco-pyranosyl (1→4)] -β-D-glucopyranosiduronic acid, and named escin IVd. Compounds **1** and **2** are geometrical isomers.

Table: ^{13}C NMR Spectral Data of Compounds **1-3** (δ Relative to TMS in pyridine-d_5, 125MHz)

C	1	2	3	C	1	2	3
1	38.2	38.2	38.3	1'	104.4	104.3	104.5
2	26.3	26.3	26.3	2'	79.4	79.5	79.5
3	90.9	90.8	90.8	3'	76.2	76.6	76.6
4	43.4	43.4	43.4	4'	81.7	81.4	82.7
5	55.8	55.8	55.9	5'	75.5	75.5	76.6
6	18.3	18.3	18.3	6'	171.5	171.9	174.4
7	32.9	32.8	33.0	1"	104.0	104.0	104.0
8	39.6	39.6	39.7	2"	75.5	75.5	75.4
9	46.5	46.5	46.5	3"	78.3	78.0	78.2
10	36.1	36.1	36.1	4"	69.5	69.5	69.5
11	23.8	23.8	23.9	5"	78.1	77.8	77.8
12	123.0	123.0	123.2	6"	61.3	61.3	61.3
13	142.3	142.2	143.1	1"'	104.4	104.3	104.2
14	41.5	41.5	41.7	2"'	74.7	74.7	74.8
15	34.4	34.4	34.6	3"'	78.1	78.3	78.0
16	67.7	68.0	68.0	4"'	71.3	71.3	71.2
17	45.9	45.7	46.6	5"'	77.8	77.8	77.6
18	41.4	41.3	40.7	6"'	62.2	62.2	62.0
19	47.2	47.2	47.6	1""	168.1	168.1	167.6
20	36.6	36.7	36.2	2""	129.6	129.1	128.0
21	76.2	76.1	75.4	3""	136.2	136.6	138.1
22	77.9	77.8	73.4	4""	13.8	15.7	15.8
23	22.3	22.2	22.3	5""	12.2	20.6	20.8
24	63.1	63.0	63.1	1""'	170.8	170.7	
25	15.4	15.3	15.4	2""'	20.6	20.7	
26	16.5	16.5	16.7				
27	27.2	27.3	27.3				
28	68.4	68.2	66.4				
29	30.0	30.0	30.4				
30	19.2	19.2	19.2				

Compound **3** was elucidated by comparison with escin IVe[2] {28-tigloyl protoaescigenin-3β-O- [β-D-glucopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)] -β-D-glucopyranosiduronic acid}. Negative-ion HRSIMS showed a quasimolecular ion peak at *m/z* 1087.5319, consistent with the molecular composition of $C_{53}H_{84}O_{23}$. The ^1H and ^{13}C NMR signals belonging to an angeloyl group instead of a tigloyl group were observed. HMBC experiment also identified C-28 esterification of the angeloyl group and the identical structure of the trisaccharide. With all the above evidences, compound **3** was established as 28-angeloylprotoaescigenin-3β-O- [β-D-glucopyranosyl (1→2)] [β-D-glucopyranosyl (1→4)] -β-D- glucopyranosiduronic acid, and named escin IVf. It is a geometrical isomer of escin IVe.

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