

## Four Triterpene Oligoglycosides from the seeds of *Aesculus Chinensis*

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**Abstract:** A pair of novel geometrically isomeric triterpenoid saponins named escins IVa and IVb, together with known escins Ia and Ib, were isolated from the seeds of *Aesculus chinensis*. Their structures were determined on the basis of spectroscopic evidences and comparison.

**Keywords:** *Aesculus chinensis*, hippocastanaceae, escins Ia, Ib, IVa, IVb, X-ray analysis.

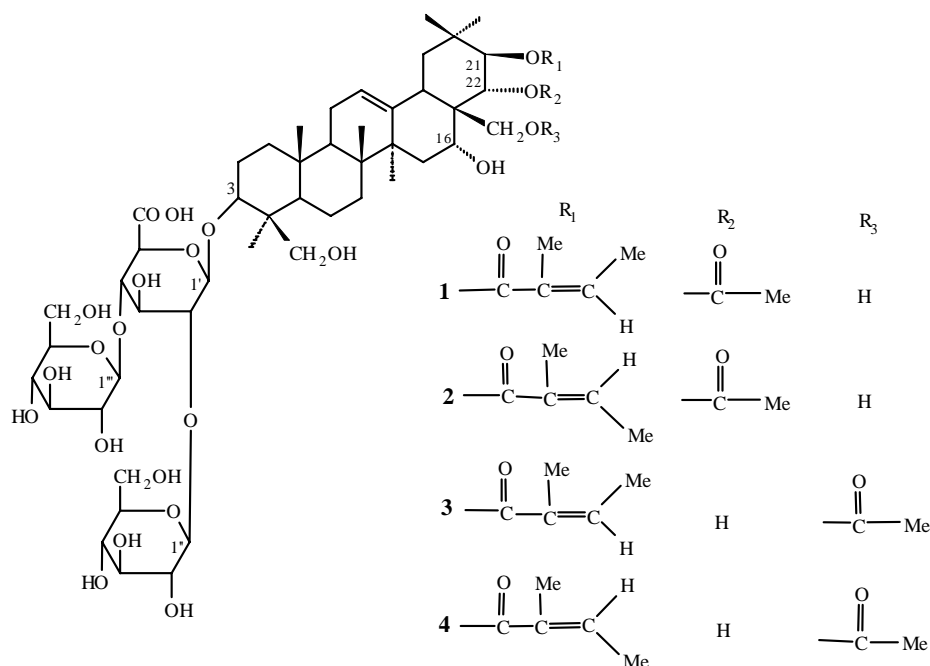
The seeds of *Aesculus chinensis* Bge. (Hippocastanaceae) have been used as folk medicine for the treatment of distension and pain in chest and abdomen<sup>1</sup>. Until now, there is no report on its chemical constituents. This paper describes structure elucidation of two new compounds, escins IVa **3** and IVb **4** on the basis of spectroscopic methods and comparison with escins Ia **1** and Ib **2**<sup>2</sup>. Among them, Escin Ia **1** was studied by X-ray diffraction analysis.

Compound **3**, white powder, showed IR bands due to carboxyl and  $\alpha,\beta$ -unsaturated ester at 1740, 1713 and 1640  $\text{cm}^{-1}$  and strong absorption bands at 3409 and 1074  $\text{cm}^{-1}$  suggestive of the oligoglycosidic structure<sup>2</sup>. The positive-mode TOF-MS of **3** displayed quasimolecular ion peaks at  $m/z$  1153  $[\text{M}+\text{Na}]^+$  and 1130  $[\text{M}]^+$  the same as **1** and **2**. <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** were similar to those of **1** with presence of a tigloyl group, an acetyl group and a trisaccharide moiety. Carbon signals of C-21, C-22, C-17 and C-28, which differed from those of **1**, were assigned as in the **Table** with aid of HMQC and HMBC spectra. The occurrence of a tigloyl group at C-21 was confirmed by the cross peak between H-21 ( $\delta$  6.40) and the carbonyl carbon ( $\delta$  168.5) of the tigloyl group in HMBC spectrum. However no correlation signal was observed between the carbonyl carbon of the acetyl group and any proton on the protoaescigenin skeleton. The position of the acetyl group at C-28 was deduced from significant shift for C-28, C-17, C-22 in <sup>13</sup>C-NMR and C<sub>28</sub>-H ( $\delta$ 4.10, d, J=9.0Hz; 4.40, d, J=9.0Hz), C<sub>21</sub>-H ( $\delta$ 6.40, d, J=10.0Hz), C<sub>22</sub>-H ( $\delta$ 4.44, d, J=10.0Hz) in <sup>1</sup>H NMR compared with those (C<sub>28</sub>-H:  $\delta$ 3.35, d, J=10.5Hz; 3.58, d, J=10.5Hz. C<sub>21</sub>-H: 6.56, d, J=10.0Hz; C<sub>22</sub>-H: 6.24, d, J=10.0Hz) of **1**.

Furthermore, the linkage site and sugar sequence were also identified by similar long-range correlations in HMBC spectrum just as in **1**: C-3 (90.9) and H-1' (4.72), C-2' (79.4) and H-1'' (5.42) and C-4' (82.6) and H-1''' (4.79). Therefore **3** was identified as 21 $\beta$ -tigloyl-28-acetylprotoaescigenin-3 $\beta$ -O- [  $\beta$ -D-glucopyranosyl (1-2) ] [  $\beta$ -D-glucopyranosyl (1-4) ] -  $\beta$ -D-glucopyranosiduronic acid, named escin IVa.

Compound **4**, white powder, showed IR bands ascribable to carboxyl and  $\alpha$ ,  $\beta$ -unsaturated ester at 1740, 1709 and 1640  $\text{cm}^{-1}$  and strong absorption bands at 3414 and 1074  $\text{cm}^{-1}$  suggestive of the oligoglycosidic structure. The negative-mode TOF-MS of **4**.

**Scheme** Structures of Escins Ia, Ib, IVa and IVb



showed quasimolecular ion peaks at  $m/z$  1152 [ $M-H+Na$ ]<sup>-</sup> and 1130 [ $M$ ]<sup>-</sup>. Comparison with <sup>1</sup>H and <sup>13</sup>C NMR spectra of **3** and **4** led to the conclusion that an angeloyl group [<sup>1</sup>H-NMR:  $\delta$  5.84 (1H, dq like, H-3'''), 1.98 (3H, d,  $J=7.0\text{Hz}$ , Ang-4''') and 1.93 (3H, s, Ang-5'''); <sup>13</sup>C-NMR: as shown in the **Table**] presented in place of a tigloyl group in the structure. Similar correlation relationships were also observed in HMBC and <sup>1</sup>H-<sup>1</sup>H NOESY spectra. Therefore, **4** was elucidated as 21 $\beta$ -angeloyl-28-acetylprotoaescigenin-3 $\beta$ -O- [  $\beta$ -D-glucopyranosyl (1-2) ] [  $\beta$ -D-glucopyranosyl (1-4) ] -  $\beta$ -D-glucopyranosiduronic acid, named escin IVb, a geometric isomer of **3**.

The existence of escins IVa and IVb in *Aesculus hippocastanum* has been foreseen by Griffini *et al*<sup>3</sup> deduced from combined LC-MS. But it was for the first time that they were fully characterized by spectroscopic methods.

**Table.** <sup>13</sup>C-NMR Data of Escins Ia, Ib, IVa and Ivb

C	Ia	Ib	IVa	IVb	C	Ia	Ib	IVa	IVb
1	38.3	38.1	38.3	38.3	29	29.4	29.2	29.4	29.6
2	26.4	26.2	26.3	26.3	30	20.0	20.0	20.0	20.1
3	90.9	90.8	90.9	91.0	1'	104.5	104.3	104.3	104.5
4	43.5	43.3	43.4	43.5	2'	79.5	78.6	79.4	79.7
5	55.9	55.8	55.9	55.9	3'	76.3	76.3	76.4	76.5
6	18.4	18.2	18.3	18.4	4'	81.7	81.9	82.6	82.6
7	33.1	32.9	33.0	33.0	5'	75.6	75.3	75.5	75.5
8	39.8	39.8	39.7	39.7	6'	170.9	170.9	170.6	170.6
9	46.6	46.4	46.5	46.6	1''	104.1	103.8	103.9	104.1
10	36.4	36.0	36.3	36.2	2''	75.6	75.3	75.5	75.5
11	23.9	23.7	23.9	23.9	3''	78.4	78.1	78.0	78.2
12	123.0	123.1	123.2	123.2	4''	69.6	69.4	69.5	69.6
13	142.7	142.5	142.6	142.5	5''	78.0	77.7	78.0	78.1
14	41.5	41.3	41.6	41.6	6''	61.4	61.3	61.4	61.4
15	34.5	34.3	34.4	34.5	1'''	104.5	104.3	104.3	104.2
16	67.9	67.7	67.4	67.5	2'''	74.8	74.6	74.8	74.7
17	47.8	47.7	46.9	46.8	3'''	78.2	77.9	78.0	78.2
18	39.9	39.6	40.4	40.4	4'''	71.4	71.1	71.2	71.2
19	47.1	46.9	46.9	46.9	5'''	77.9	77.5	77.8	77.8
20	36.2	36.0	36.2	36.0	6'''	62.2	61.9	62.0	61.9
21	79.3	79.3	81.4	81.0	1''''	167.9	167.6	168.5	168.4
22	74.1	74.6	71.0	70.9	2''''	129.3	128.6	129.6	129.3
23	22.3	22.2	22.3	22.3	3''''	136.8	137.0	136.2	136.1
24	63.2	63.0	63.1	63.1	4''''	14.1	15.3	14.0	15.8
25	15.4	15.7	15.4	15.4	5''''	12.3	20.8	12.3	20.9
26	16.6	16.4	16.7	16.7	1'''''	170.9	170.9	170.6	170.6
27	27.3	27.1	27.2	27.3	2'''''	20.8	20.8	20.6	20.7
28	63.6	63.5	66.3	66.3					

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