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A New Triterpenoid Oligoglycoside Escin IVe from the Seeds of *Aesculus Chinensis*

Jing ZHAO[1], Xiu Wei YANG[1]*, Yu Xin CUI[1], Xue Hui LIU[1], Shun He OUYANG[2]

[1]National Laboratory of Natural and Biomimetic Drugs, Beijing Medical University, Beijing 100083

[2]Yantai Luye Pharmaceutical Co. Ltd., 43 Yingbin Road, Yantai, Shandong 264001

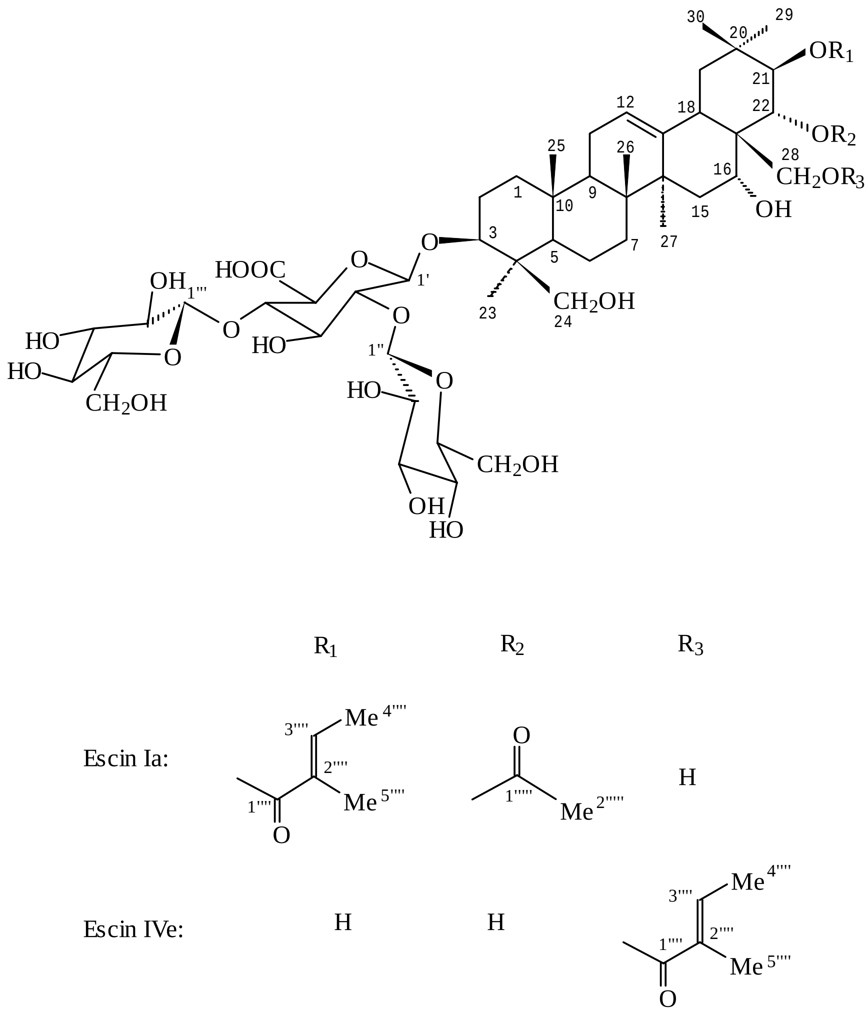
Abstract: A new triterpenoid saponin named escin Ⅳe was isolated from the seeds of *Aesculus chinensis*. Its structure was established as 28-tigloylprotoaescigenin-3β-O-[β-D-glucopyranosyl (1-2)] [β-D-glucopyranosyl (1-4)] -β-D-glucopyranosiduronic acid.

Keywords: *Aesculus chinensis*; hippocastanaceae; triterpenoid saponins; escin Ⅳe.

In the course of our studies on new biologically active saponins of natural medicines, we have isolated escins Ia, Ib, IVa, IVb, IVc, and IVd from seeds of *Aesculus chinensis* Bge.(Hippocastanaceae), and single crystal X-ray diffraction analysis was undertaken on escin Ia[1], which confirms the absolute configuration and sugar sequence. The present paper describes the structure determination of a new triterpenoid saponin named escin IVe from the same plant.

Escin IVe, white powder. Positive-mode TOF-MS: m/z 1111 $[M + Na]^+$, coupled with NMR data, corresponds to an empirical formula of $C_{53}H_{84}O_{23}$. The IR spectrum showed absorption bands due to carboxyl and α, β-unsaturated ester at 1731，1708，1653 and 1649 cm^{-1} and broad bands at 3404， 1072 cm^{-1} suggestive of oligoglycosidic structure[2]. ^1H and ^{13}C NMR signals were assigned with the aid of HMQC, HMBC, ^1H-^1H COSY, and NOESY spectra and by comparison with those of escin Ia which is a pentacyclic triterpene saponin having an olean-12-ene skeleton bearing oxygenated functions at C-3, C-16, C-21, C-22, C-24 and C-28. Characteristic signals owing to a protoaescigenin skeleton, a tigloyl group [^1H-NMR: δ 6.94 (1H, *dq*-like, H-3''''), 1.51 (3H, d, J=5.5Hz, H-4'''') and 1.76 (3H, s, H-5''''); ^{13}C-NMR: see **Table 1**] and a trisaccharide moiety were observed. However, the chemical shifts of C-17, C-21, C-22 and C-28 together with corresponding protons differed from those of escin Ia (see **Table 1**). The location of the tigloyl group at C-28 was deduced from long-range correlation peaks between the carbonyl carbon of the tigloyl group and Ha,b-28 in HMBC spectrum and cross peaks between the Me-5'''' and Ha,b-28 in ^{1}H-^{1}H NOESY spectrum.

Scheme. Structures of Escins Ia and Ive



The sugar unit includes three monosaccharides as demonstrated in the HMBC spectrum by three anomeric carbon signals at δ 104.4, 104.0 and 104.4 crossed with anomeric protons at δ 4.84 (1H, d, J=7.0Hz, H-Glc A-1′), 5.56 (1H, d, J=7.5Hz, H-Glc-1″) and 5.16 (1H, d, J=8.0Hz, H-Glc-1‴), respectively. The large J values indicated β-glycosidic linkages in all cases, identical with those of escin Ia. On mild acid hydrolysis, escin IVe yielded glucose and glucuronic acid. HMBC (correlations between H-3 and C-1'; C-3 and H-1'; C-2' and H-1''; and C-4' and H-1''') and ^{1}H-^{1}H NOESY (cross peaks between H-3 and H-1'; H-2' and H-1''; and H-4' and H-1''') experiments also verified the glycosidation position and the sugar sequence. With all the above evidences, the structure of escin IVe was established as 28-tigloyl-protoaescigenin-3β-O- [β-D-glucopyranosyl (1-2)] [β-D-glucopyranosyl (1-4)] -β-D-glucopyranosiduronic acid.

Table 1. ^{13}C NMR Spectra Data for Escins IVe and Ia

C	IVe	Ia [1]	C	IVe	Ia
1	38.3	38.3	1'	104.4	104.5
2	26.3	26.4	2'	79.4	79.5
3	90.9	90.9	3'	76.3	76.3
4	43.4	43.5	4'	81.7	81.7
5	55.9	55.9	5'	75.7	75.6
6	18.3	18.4	6'	172.2	172.2
7	33.0	33.1	1''	104.0	104.1
8	39.7	39.8	2''	75.5	75.6
9	46.6	46.6	3''	78.3	78.4
10	36.2	36.4	4''	69.5	69.6
11	23.9	23.9	5''	77.1	78.0
12	123.0	123.0	6''	61.3	61.4
13	143.1	142.7	1'''	104.4	104.5
14	40.7	41.5	2'''	74.4	74.8
15	34.5	34.5	3'''	78.3	78.2
16	67.9	67.9	4'''	71.3	71.4
17	46.6	47.8	5'''	77.8	77.9
18	41.7	39.9	6'''	62.1	62.2
19	47.5	47.1	1''''	167.7	167.9
20	36.1	36.2	2''''	129.0	129.3
21	77.8	79.3	3''''	136.9	136.8
22	73.4	74.1	4''''	14.0	14.1
23	22.3	22.3	5''''	12.1	12.3
24	63.1	63.2	1'''''		170.9
25	15.4	15.4	2'''''		20.8
26	16.7	16.6			
27	27.2	27.3			
28	66.7	63.6			
29	30.4	29.4			
30	19.2	20.0			

References

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