afforded methyl 2,3-di-O-benzyl-L-*arabino*-pentodialdo-1,4-furanoside (XIII) (α-anomer (XIIIa). semicarbazone, m.p. 121~124°, $[\alpha]_D^{20}$ −46.4° (c=1.14, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{25}O_5N_3$: C, 63.14; H, 6.31; N, 10.52. Found: C, 63.18; H, 6.22; N, 10.28. β-anomer (XIIIb). semicarbazone, m.p. 154~156°, $[\alpha]_D^{20}$ +20.1° (c=2.10, $CHCl_3$). Found: C, 62.86; H, 6.37; N, 10.69), which was confirmed to be identical with the one derived from D-glucose series as already described.

Finally, XIIIb was condensed with nitromethane in absolute methanol containing sodium methoxide, and epimeric mixture of 6-deoxy-6-nitro-L-*arabino*-hexofuranoside (XVIII) (*Anal.* Calcd. for $C_{21}H_{25}O_7N$: C, 62.52; H, 6.25; N, 3.47. Found: C, 62.48; H, 6.36; N, 3.45) was obtained. Separation of epimeric mixture and the study on derivatives of XVIII are being undertaken.

The authors are greatly indebted to Dr. G. Sunagawa for giving us permission for this publication, to Drs. I. Iwai, H. Okazaki, H. Watanabe for their helpful suggestions and encouragements, and also to Mr. Y. Shimada for his technical assistance.

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Received July 16, 1966

[Chem. Pharm. Bull. 15(1) 135~137 (1967)]

UDC 581.19 : 547.597 : 582.772.3

On the Triterpenic Constituents of the Seeds Saponin of *Aesculus turbinata* BLUME.

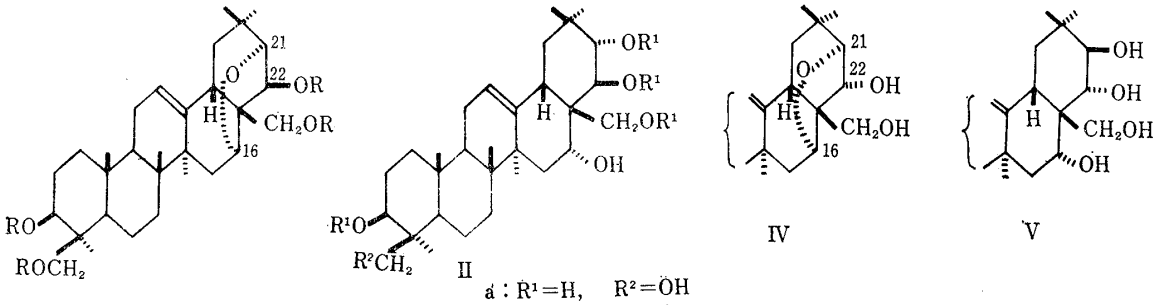
During the course of the chemical and some biological studies on several kinds of saponins and sapogenins, which have been undertaken in this laboratory for these years, it has become an important need to investigate the triterpenic sapogenins of the seeds of *Aesculus turbinata* BLUME (トチノキ).

Tschesche, *et al.*[1] proposed the whole structure of aescin, a saponin originated from the seeds of *Aesculus hippocastanum* L. (セイヨウトチノキ), while Jeger, *et al.*[2] revealed the structure of its genin, aescigenin as being 3β,22β,24,28-tetrahydroxy-16α,21α-epoxy-olean-12-ene (Ia) and assumed that it must be derived from a genuine sapogenin, 3β,16α,21α,22β,24,28-hexahydroxy-olean-12-ene (IIa). Several years later, Kuhn and Loew[3] supported the assumption by isolating protoaescigenin (IIa) on mild hydrolysis of the above mentioned saponin. Furthermore, Kuhn and Loew[4] obtained aescinidin, a minor sapogenin, occurring in the hydrolysate of the total saponin, which was proved later on, by Tschesche and Wulff,[5] to be identical with barringtogenol C, previously isolated from the fruits saponin of *Barringtonia actangula* GAERTN. and established as III by Barua and Chakrabarti.[6]

1) R. Tschesche, U. Axen, G. Snatzke: Liebig's Ann., **669**, 171 (1963).
2) G. Cainelli, A. Melera, D. Arigoni, O. Jeger: Helv. Chim. Acta, **40**, 2390 (1957).
3) R. Kuhn, I. Loew: Liebig's Ann., **669**, 183 (1963).
4) *Idem*: Tetrahedron Letters, **1964**, 891.
5) R. Tschesche, G. Wulff: *Ibid.*, **1965**, 1569.
6) A. K. Barua, P. Chakrabarti: Tetrahedron, **21**, 381 (1965).

Concerning to the saponin of the Japanese *Aesculus* seeds, on the other hand, Kariyone and Tobinaga reported in 1958 the isolation[7] and some chemical investigations[8] of the sapogenin, which they recognized being non-identical with aescigenin. However, the conclusive evidence for the chemical structure of the sapogenin has never been provided. In the present communication, the authors wish to report the isolation, identification, and a comment on the chemical constituents of the triterpenic sapogenins of the Japanese *Aesculus* seeds.

On a mild acid treatment (refluxed for 2 hrs. in a 1:1 mixture of 4*N* hydrochloric acid and ethanol), followed by alkaline hydrolysis (refluxed for 1 hr. in 5% potassium hydroxide methanol), the saponin isolated from the methanol extract of the seeds by usual procedure fractionating with butanol afforded a genin-mixture, whose thin-layer chromatogram (silica gel G, Merck) showed four main spots with Rf values of 0.17, 0.23, 0.30, and 0.36, respectively by using a chloroform-methanol (6:1) mixture as a developing solvent. The spots were tentatively designated as R_P, R_B, R_A, and R_X, and the separation of these components was achieved by Al_2O_3 column chromatography, with the yields of 50% (R_P), 3% (R_B), 7.8% (R_A), and 0.8% (R_X) based on the total genin-mixture. The respective identities of R_P, R_B-tetraacetate, and R_A-tetraacetate with protoaescigenin, aescinidin-tetraacetate, and aescigenin-tetraacetate were established by their direct comparisons through the courtesy of Prof. Tschesche to whom the authors' deepest thanks are due.



I
a : R=H aescigenin
b : R=Ac

II
a : R¹=H, R²=OH protoaescigenin
b : R¹=Ac, R²=OAc

III R¹=R²=H aescinidin (=barringtogenol C)

IV

V

Chart 1.

The observations described here reveal the quite resemblance of the triterpenic constituents*1 between the Japanese and European *Aesculus* seeds saponins.

In connection with our studies on the chemical structures of theasapogenols A[9] and B,[10] the nuclear magnetic resonance analyses were made on the acetyl derivatives of aescigenin and protoaescigenin (Ib and IIb), and also on some other derivatives. The results led us to revise the configuration of aescigenin (Ia) and protoaescigenin (IIa), from 22β-OH and 21α,22β-glycol to 22α-OH and 21β, 22α-glycol, respectively (IV and V, as shown in Chart 1), which will be discussed in detail elsewhere.[11]

*1 The comparison of both of the total genin-mixtures on thin-layer chromatography (TLC) disclosed that they consist of almost identical genin components except the European sapogenin mixture contains one more minor spot at the lowest portion on TLC.

7) T. Kariyone, S. Tobinaga : Yakugaku Zasshi, **78**, 531 (1958).
8) S. Tobinaga : *Ibid.*, **78**, 534 (1958).
9, 10) I. Yosioka, T. Nishimura, A. Matsuda, I. Kitagawa : Tetrahedron Letters, **1966**, 5979, 5973.
11) I. Yosioka, T. Nishimura, A. Matsuda, K. Imai, I. Kitagawa : *Ibid.*, **1967**, No. 7(in press).

The chemical structure of R_X is at present under study in this laboratory.

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Received September 28, 1966