gave a ketone (XX), $C_{29}H_{46}O_6$, m.p. 215°, $[\alpha]_D^{19}$ −11.2°, IR ν_{max}^{Nujol} : 1733 cm^{-1}, ORD : a=−33°, indicating it to be in the type of coprostan-3-one and not of 1-oxo or 4-oxo isomer.[7,8] Accordingly, D-glucose in II should be linked with the hydroxyl group at C-3 of the aglycone. These results with the application of Klyne rule as mentioned above, revealed that glucoconvallasaponin-B (II) may be formulated as convallagenin-B-(3)-β-D-glucopyranosido, (5)-α-L-arabopyranoside.

Although bufotoxin has been considered to have suberyl-arginate group at C-14,[11] II is the first steroidal glycoside shown to have the sugar moiety combined at the angular position of C-5. No other saponin having sugar moieties at the different positions within a steroidal nucleus has also ever been found than those such as I and II, except the triterpenoid saponins recently reported.[12]

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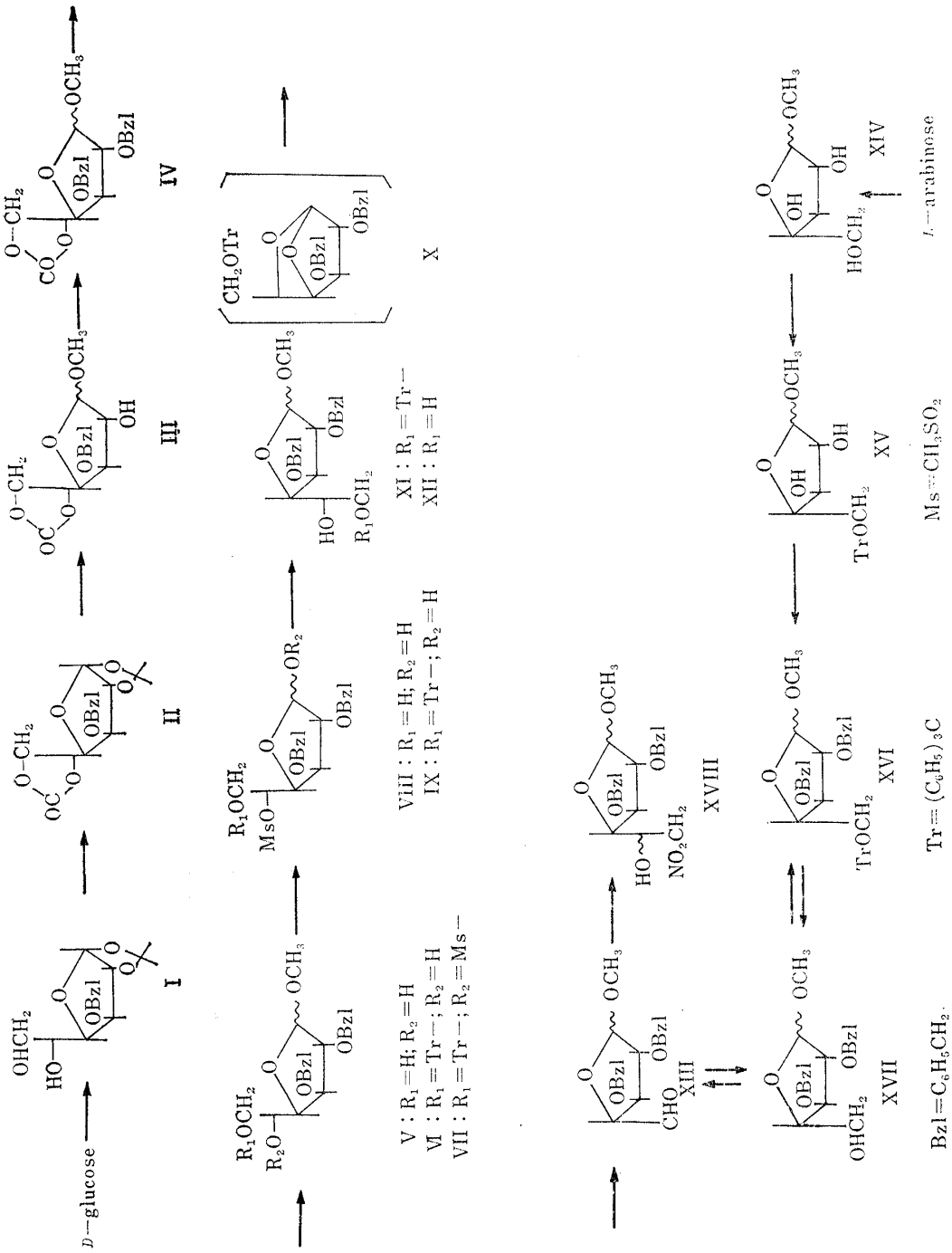
Rearrangement of D-glucofuranoside to L-*Arabino*-hexofuranoside

(Synthesis of 6-Deoxy-6-nitro-L-*arabino*-hexofuranoside through L-*Arabino*-pentodialdo-1,4-furanoside from D-Glucose or L-Arabinose)

This communication deals with the rearrangement of 2,3-di-O-benzyl-5-O-mesyl-6-O-trityl-D-glucofuranose (IX) to methyl 2,3-di-O-benzyl-6-O-trityl-L-*arabino*-hexofuranoside (XI), and the conversion of XI into methyl 2,3-di-O-benzyl-L-*arabino*-pentodialdo-1,4-furanoside (XIII). 6-Deoxy-6-nitro-L-*arabino*-hexofuranoside has been synthesized from XIII as illustrated in the following chart. In order to get IX, 1,2-O-isopropylidene-3-O-benzyl-D-glucofuranose (I),[1] easily obtainable from D-glucose, was served as starting material.

Treatment of I with phosgene in pyridine gave 1,2-O-isopropylidene-3-O-benzyl-D-glucofuranose 5,6-carbonate (II) (m.p. 119~120°, $[\alpha]_D^{28}$ −53° (c=3.7, $CHCl_3$). *Anal.* Calcd. for $C_{17}H_{20}O_7$: C, 60.71; H, 5.99. Found : C, 60.34; H, 5.96), which was followed by methanolysis with 1.2% (v/v) methanolic sulfuric acid to afford the anomeric mixture of methyl 3-O-benzyl-D-glucofuranoside 5,6-carbonate (III) (α-anomer (IIIa), m.p. 62~63°, $[\alpha]_D^{29}$ +93.3° (c=2.7, MeOH). *Anal.* Calcd. for $C_{15}H_{18}O_7$: C, 58.06; H, 5.85. Found : C, 57.69; H, 5.89. β-anomer (IIIb), syrup, $[\alpha]_D^{30}$ −61.2° (c=3.3, MeOH). Found : C, 57.79; H, 6.05). Benzylation of III with benzylchloride and silver oxide in dimethylformamide, gave methyl 2,3-di-O-benzyl-D-glucofuranoside 5,6-carbonate (IV) (α-anomer (IVa), syrup, $[\alpha]_D^{27}$ +97.5° (c=3.3, $CHCl_3$). *Anal.* Calcd. for $C_{22}H_{24}O_7$: C, 66.00; H, 6.05. Found: C, 65.15; H, 6.00. β-Anomer (IVb), syrup, $[\alpha]_D^{27}$ −52.5° (c=3.20, $CHCl_3$). Found : C, 65.71;

1) A.S. Meyer, T. Reichstein : Helv. Chim. Acta, **29**, 156 (1946).



H, 6.18). Hydrolysis of Ⅳb with aqueous acetone solution of 0.33*N* barium hydroxide afforded methyl 2,3-di-O-benzyl-β-D-glucofuranoside (Ⅴ) (m.p. 59~61°, $[\alpha]_D^{27}$ −59.3° (c=2.7, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{26}O_6$: C, 67.36; H, 7.00. Found : C, 67.15; H, 6.73). Tritylation of Ⅴ followed by mesylation of the resulting tritylated compound (Ⅵ) with methanesulfonyl chloride in pyridine gave the syrupy substance, methyl 2,3-di-O-benzyl-5-O-mesyl-6-O-trityl-β-D-glucofuranoside (Ⅶ) ($[\alpha]_D^{28}$ +4.7° (c=3.0, $CHCl_3$). *Anal.* Calcd. for $C_{41}H_{42}O_8S$: C, 70.87; H, 6.09; S, 4.61. Found: C, 70.89; H, 6.25; S, 4.52).

Hydrolysis of Ⅶ in aqueous acetone solution of sulfuric acid ($(CH_3)_2CO$-H_2O-H_2SO_4 =10:5:1) at 60° resulted the formation of 2,3-di-O-benzyl-5-O-mesyl-D-glucofuranose (Ⅷ) (m.p. 104~108°, $[\alpha]_D^{20}$ +15.6° (c=3.8, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{26}O_8S$: C, 57.52; H, 5.98; S, 7.31. Found : C, 57.37; H, 6.06; S, 7.56). Tritylation of Ⅷ in dimethylformamide in the presence of silver oxide yielded 2,3-di-O-benzyl-5-O-mesyl-6-O-trityl-D-

glucofuranose (IX) (m.p. 119~121°, $[\alpha]_D^{20}$ +23.2° (c=2.43, $CHCl_3$). *Anal.* Calcd. for $C_{40}H_{40}O_8S$: C, 70.57; H, 5.92; S, 4.71. Found: C, 70.38; H, 5.76; S, 4.94). Rearrangement of IX in absolute methanol solution of 1~2 mole sodium methoxide yielded the syrupy anomeric mixture of methyl 2,3-di-O-benzyl-6-O-trityl-L-altrofuranoside (XI)*1 (*Anal.* Calcd. for $C_{40}H_{40}O_6$: C, 77.89; H, 6.53. Found: C, 77.61; H, 6.49), which was difficult to separate by chromatographic procedure, besides, a crystalline compound (m.p. 98~99.5°, $[\alpha]_D^{20}$ +16.1° (c=2.52, $CHCl_3$). IR (Nujol): no OH, C=O and OSO_2R. NMR (τ) (in $CDCl_3$): 2.4~2.8 (25H, $5C_6\underline{H}_5$), 5.46 (4H, $2C\underline{H}_2C_6H_5$), 4.5~7.3 (7H, no $OC\underline{H}_3$ and $SO_2C\underline{H}_3$). *Anal.* Calcd. for $C_{39}H_{36}O_5$: C, 80.11; H, 6.21. Found: C, 80.06; H, 6.14) corresponding to the formula (X) was obtained.

XI was treated with aqueous acetone solution of acetic acid ($AcOH-H_2O-(CH_3)_2CO$=17:7:3). The resulted product was chromatographed on silica gel, eluting with chloroform initially, then with the solvent mixture (AcOEt-hexane=2:3) to separate the anomeric mixture of methyl 2,3-di-O-benzyl-L-altrofuranoside (XII) (α-anomer (XIIa), syrup, $[\alpha]_D^{20}$ −55.8° (c=2.69, $CHCl_3$). *Anal.* Calcd. for $C_{21}H_{26}O_6\cdot\frac{1}{4}H_2O$: C, 66.56; H, 7.05. Found: C, 66.50; H, 6.94. β-anomer (XIIb), glassy amorphous solid, $[\alpha]_D^{20}$ +55.5° (c=2.73, $CHCl_3$). Found: C, 66.59; H, 7.08).

Oxidation of XIIb with lead tetraacetate in benzene gave methyl 2,3-di-O-benzyl-β-L-*arabino*-pentodialdo-1,4-furanoside (XIIIb), the structure of which was confirmed by the comparison of its semicarbazone, m.p. 154~156°, with the authentic sample obtained by oxidation of methyl 2,3-di-O-benzyl-β-L-arabinofuranoside (XVIIb) as described below.

Also XIIIa, yielded by lead tetraacetate oxidation of XIIa, gave likewise the same semicarbazone, m.p. 121~124°, as the authentic sample derived from methyl 2,3-di-O-benzyl-α-L-arabinofuranoside (XVIIa). Further, XIIIa from XIIa was reduced to XVIIa with sodium borohydride, followed by tritylation to give the identical methyl 2,3-di-O-benzyl-5-O-trityl-α-L-arabinofuranoside (XVIa) with the one derived from L-arabinose.

On the other hand, in order to get XIII from L-arabinose series, methyl L-arabinofuranoside (XIV)[2] was tritylated in pyridine to give methyl 5-O-trityl-L-arabinofuranoside (XV)*2 (α-anomer (XVa), m.p. 112~113°, $[\alpha]_D^{26}$ −89.1° (c=3.10, $CHCl_3$), $[\alpha]_D^{27}$ −66.7° (c=3.05, AcOEt). *Anal.* Calcd. for $C_{25}H_{26}O_5$: C, 73.87; H, 6.45. Found: C, 74.06; H, 6.37. β-anomer (XVb), m.p. 122~123°, $[\alpha]_D^{27}$ +50.9° (c=3.02, $CHCl_3$). Found: C, 73.83; H, 6.48), followed by benzylation to afford methyl 2,3-di-O-benzyl-5-O-trityl-L-arabinofuranoside (XVI) (α-anomer (XVIa), m.p. 80~81°, $[\alpha]_D^{27}$ −41.2° (c=3.3, $CHCl_3$). *Anal.* Calcd. for $C_{39}H_{38}O_5$: C, 79.84; H, 6.53. Found: C, 79.69; H, 6.48. β-anomer (XVIb), syrup, $[\alpha]_D^{27.5}$ +31.3° (c=2.94, $CHCl_3$). Found: C, 80.07; H, 6.33).

Treatment of XVI with 80% acetic acid gave the syrupy substance, methyl 2,3-di-O-benzyl-L-arabinofuranoside (XVII) (α-anomer (XVIIa), syrup, $[\alpha]_D^{27}$ −88.4° (c=3.83, $CHCl_3$). *Anal.* Calcd. for $C_{20}H_{24}O_5$: C, 69.75; H, 7.02. Found: C, 69.47; H, 7.10. β-anomer (XVIIb), syrup, $[\alpha]_D^{24.5}$ +43.0° (c=2.61, $CHCl_3$). Found: C, 69.48; H, 7.07). Oxidation of XVII with dicyclohexylcarbodiimide and 100% phosphoric acid in dimethyl sulfoxide[3]

*1 P.A. Levene, *et al.* (P.A. Levene, J. Compton: J. Biol. Chem., **116**, 169 (1936)), B.R. Baker, *et al.* (E.J. Reist, L. Goodman, R.R. Spencer, B.R. Baker: J. Am. Chem. Soc., **80**, 3962 (1958)), and J.S. Brimacombe *et al.* (J.S. Brimacombe, M. Stacey, L.C.N. Tucker: J. Chem. Soc., 5391 (1964)) obtained methyl 6-deoxy-2,3-O-isopropylidene-β-D-allofuranoside, stereospecifically from 2,3-O-isopropylidene-5-O-tosyl-L-rhamnofuranose under the same condition. If the reaction of IX proceeds through the same mechanism which they proposed, the resulted product is expected to be methyl 2,3-di-O-benzyl-6-O-trityl-L-altrofuranoside.

*2 During this investigation, H.G. Fletcher, Jr., *et al.* (C.P.J. Glaudemans, H.G. Fletcher, Jr.: J. Am. Chem. Soc., **87**, 4636 (1965)) reported the antipode of XVa, methyl 5-O-trityl-α-D-arabinofuranoside, m.p. 112~113°, $[\alpha]_D^{20}$ +62.4° (c=1.56, AcOEt).

2) I. Augestad, E. Berner: Acta. Chem. Scand., **8**, 251 (1954).

3) K.E. Pfitzner, J.G. Moffatt: J. Am. Chem. Soc., **85**, 3028 (1963). *Ibid.*, **87**, 5661, 5670 (1965).

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.

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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]

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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).