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THE STRUCTURES OF ARALOSIDES A AND B

N.K. Kochetkov, A.J. Khorlin and V.E. Vaskovsky

Institute for Chemistry of Natural Products

U.S.S.R. Academy of Sciences, Moscow

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IT is known that tissue extracts of Aralia family plants exhibit a specific tonic effect on man and mammals. We have recently isolated[1] three individual physiologically active saponines from Aralia manschurica roots, named aralosides A, B and C. The present communication contains data which can serve a basis for suggesting structures I and II for aralosides A and B respectively.

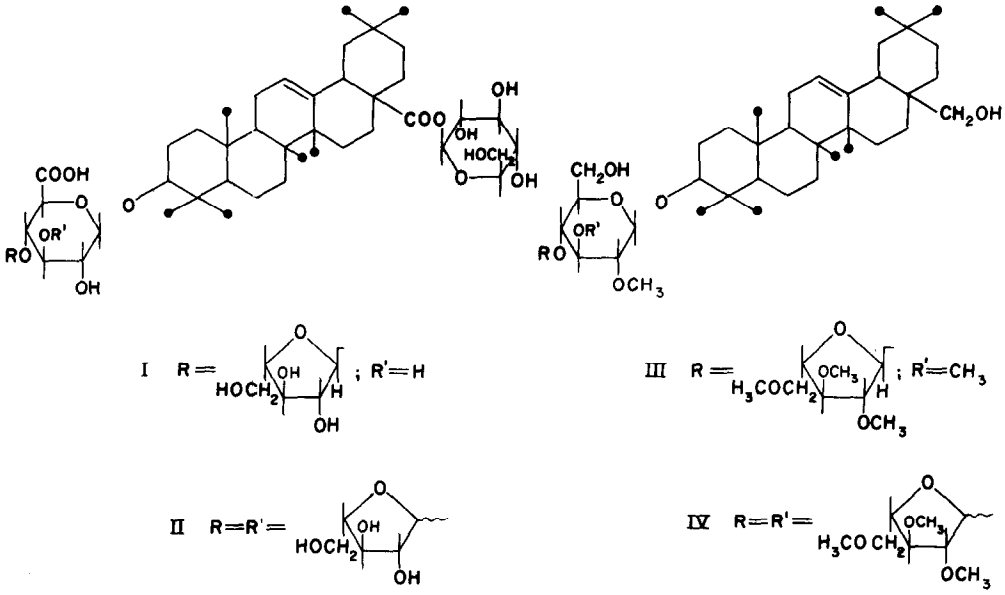
It has already been noted,[1] that araloside A is an oleanolic acid trioside, containing residues of one glucose, one arabinose and one glucuronic acid, whereas araloside B is a tetroside of the same aglicone with the sugar moiety containing residues of one glucose, two arabinose and one glucuronic acid.

The use of ion exchange resins made it possible to obtain araloside A in an analytically pure state, m.p. 195-196° (from CH_3OH, dec.), $[\alpha]_D^{20}$ -26.7° (c 1.9 in CH_3OH). (Found: C, 60.53, 60.65; H, 8.34, 8.24; Calc. for $C_{47}H_{74}O_{18}$: C, 60.88; H, 8.04%).

Methylation of I with CH_3I in the presence of Ag_2O or $Ba(OH)_2$ in dimethylformamide[2] leads to an amorphous permethyl-I, $[\alpha]_D^{20}$ -19.3° (c 1.96 in $CHCl_3$). (Found: C, 64.17, 64.37; H, 8.93, 8.93; Calc. for $C_{57}H_{94}O_{18}$: C, 64.14; H, 8.88%). II gives amorphous permethyl-II under similar con-

[1] N.K. Kochetkov et al., J. Gen. Chem. (U.S.S.R.) 30, 658 (1960).

[2] R. Kuhn et al., Angew. Chem. 72,(22), 39 (1960).



ditions, $[\alpha]_D^{20}$ -12.6° (c 4.0 in $CHCl_3$). (Found: C, 62.79, 62.79; H, 8.69, 8.57; Calc. for $C_{64}H_{106}O_{22}$: C, 62.62; H, 8.70%).

Reduction of permethyl-I with $LiAlH_4$ in ether under reflux (15 hr) leads to the formation of 2,3,4,6-tetramethyl-D-sorbitol, and a partially methylated erythrodiol bioside, III, $[\alpha]_D^{20}$ -1.9° (c 4.7 in $CHCl_3$). (Found: C, 68.60, 68.77; H, 9.74, 9.67; Calc. for $C_{45}H_{76}O_{11}$: C, 68.62; H, 9.51%). Permethyl-II can be similarly reduced to 2,3,4,6-tetramethyl-D-sorbitol and a partially methylated erythrodiol trioside, IV, $[\alpha]_D^{20}$ -2.5° (c 4.1 in $CHCl_3$). (Found: C, 65.86, 65.67; H, 9.35, 9.42; Calc. for $C_{53}H_{90}O_{15}$: C, 65.81; H, 9.38%).

The results of this reduction indicate that the D-glucopyranose residue in I as well as in II is attached to either the genine or the glucuronic

acid carboxyl. In order to determine the position of the glucose residue the following experiments were carried out.

Methylation of I with diazomethane in ethereal-alcoholic solution afforded a monomethyl ester which on hydrolysis gave oleanolic acid. Treatment with $Ba(OH)_2$ (30 min, 50°; under these conditions I and II do not alter) hydrolysed the monomethyl ester of I to I. Similar results were obtained in an analogous treatment of II. These data indicate, that the glucose residue in I and II is joined to the oleanolic acid carboxyl, methyl oleanolate being very stable towards acid and alkaline hydrolysis.[3] The difference in molecular rotation of I and III on one hand and II and IV on the other indicates that the D-glucopyranose residue in both I and II is attached to the carboxyl group by means of a β-glucosidic bond.

2,3,5-Trimethyl-L-arabinose and 2,3-dimethyl-D-glucose were identified among the products of hydrolysis of III (5% $HClO_4$ in CH_3OH, 3-4 hr at 100° and subsequent treatment with aq. $HClO_4$). IV hydrolysate contained 2,3,5-trimethyl-L-arabinose and 2-methyl-D-glucose. This leads to the conclusion, that the hydrogen atom of the oleanolic acid hydroxyl in I is substituted for a glucuronic acid residue the latter being bound to an L-arabinose residue at position 4 or 5. In II two L-arabinose residues are bound to the glucuronic acid, one at position 3 and the other at position 4 or 5.

In order to determine the positions of the arabofuranosyl residues, and consequently the size of the oxide ring of the glucuronic acid residue, I and II were subjected to partial hydrolysis (2% aq. H_2SO_4, 90-100°, 5 hr). The same progenine was isolated from both hydrolysates. This was oleanolic acid β-D-glucuronoside, characterized by its dimethyl ester, m.p. 200-205° (dec.), $[\alpha]_D^{20}$ +11.5° (c 2.3 in $CHCl_3$). (Found: C, 68.72; H, 9.32; Calc. for $C_{38}H_{60}O_9$: C, 69.06; H, 9.15%). Reduction of the dimethyl ester with

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[3] E. Hardegger et al., Helv. Chim. Acta 35, 824 (1952).

$LiAlH_4$ (8 hr under reflux in ether-tetrahydrofuran) lead to erythrodiol 3-β-D-glucoside, $[\alpha]_D^{20}$ +31.5° (c 3.5 in ethanol) which gave glucose and erythrodiol on hydrolysis. Methylation of the erythrodiol glucoside with subsequent hydrolysis of the permethyl derivative affords 2,3,4,6-tetramethyl-D-glucose. Hence one may conclude that the glucuronic acid residue is present in I and II as a pyranose form; the latter carries an L-arabinose residue at position 4 in I and one of the L-arabinose residues at the same position in II. Molecular rotation of the progenine and its erythrodiol indicate that in I as well as in II the glucuronic acid residue is attached to the aglycone by means of a β-glycosidic bond.

An analysis of the molecular rotations showed that the L-arabofuranosyl residue in I is in the α-configuration. The configuration of the arabinose residues in II requires further clarification.