[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

Glycofuranosides and Thioglycofuranosides. III. New Crystalline Furanosides of *d*-Galactose and *l*-Arabinose

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In Part I of this series[2] the synthesis of β-ethylgalactofuranoside by the reaction of the ethylmercaptal of the sugar with mercuric chloride in alcohol solution under neutral conditions was described. The isolation of the α-isomer[3] in crystalline form was also presented. This method has now been extended with success to other alcohols and also to the pentose *l*-arabinose. Three new β-alkylgalactofuranosides and two α-alkylarabinofuranosides have been prepared in crystalline form, and they are listed with their physical properties in Table I.

These substances, with the exception of β-benzylgalactofuranoside, are very hygroscopic. The yields are mostly low, as the presence of even a small amount of the other isomer seems to hinder crystallization very strongly. The β-propylgalactofuranoside crystallizes spontaneously, with a good yield. The α-methyl *l*-arabinofuranoside sirup was crystallized by seeding with its mirror image, crystalline α-methyl-*d*-arabinofuranoside.[4]

Galactose ethylmercaptal reacts quite slowly with benzyl alcohol and the resulting sirup has a smaller negative rotation than those of the other reaction sirups.

Attempts to prepare an intermediate thioarabinofuranoside, analogous to the thioglucosides,[2,5] failed, so the formation of the arabinofuranosides must be similar to that of the galactofuranosides.

As shown in Table I, the rotations of all these furanosides agree satisfactorily with the rotations calculated on the basis of Hudson's isorotation rules.

The $B_{(1-4)}$ value for the galactofuranosides was calculated from the molecular rotations for α- and β-ethylgalactofuranosides; the respective A_x values for the galactofuranosides were calculated from the molecular rotations of the galactopyranosides. The $B_{(1-4)}$ value for the *l*-arabinofuranosides was calculated from the molecular rotation of α-methyl-*d*-arabinofuranoside; the respective A_x^0 values for the *l*-arabinofuranosides were calculated from the molecular rotations of the *l*-arabinopyranosides.

Experimental

Preparation of β-Methylgalactofuranoside.—A mixture of 5.7 g. of galactose ethylmercaptal, 10.9 g. of mercuric chloride (2 moles), 5 g. of yellow mercuric oxide, and 3 g. of drierite was shaken with 60 cc. of absolute methyl alcohol for four hours at room temperature. The mixture was filtered, the filtrate treated with 5 cc. of pyridine and kept at 0° for two hours. The pyridine-mercuric chloride was filtered off and the filtrate evaporated *in vacuo* at 40° to a sirup. The sirup was dissolved in cold water, the solution filtered and neutralized with a few drops of sodium hydroxide solution to phenolphthalein, then evaporated *in vacuo* at 40° to a sirup. After several evaporations from absolute ethyl alcohol, the sirup was extracted with dry ether on a shaking machine. About four liters of solvent was used and the resulting solution was distilled off from a bath at 40–50°. The sirup left was dissolved in a small amount of absolute methyl alcohol and the solution filtered and concentrated to a hard sirup in a vacuum desiccator over calcium chloride. The sirup, rotating −83° in water solution, was then kept in an icebox and after one month changed to a solid crystalline mass.

The latter was dissolved in 100 cc. of warm ethyl acetate and the solution seeded at 0°. Crystals were slowly deposited in the form of hard buttons. On further recrystallization from ethyl acetate pure crystals were obtained: yield 20%; m. p. 63–65°, $[\alpha]^{20}\mathrm{D}$ −108° (0.0500 g. substance, 3 cc. of water solution, 2-dm. semi-micro tube, rotation 3.60° to the left). The crystals did not reduce Fehling's solution and were quite hygroscopic. The mother liquor slowly deposited more crystalline material.

Anal. Calcd. for $C_7H_{14}O_6$: C, 43.3; H, 7.2. Found: C, 43.1; H, 7.1.

Preparation of β-Propylgalactofuranoside.—A mixture of 5.7 g. of galactose ethylmercaptal, 10.9 g. of mercuric chloride (2 moles), 5 g. of yellow mercuric oxide, and 3 g. of drierite was shaken with 60 cc. of absolute *n*-propyl alcohol for five hours at room temperature. The mixture was filtered and worked up as in the preparation of the methylgalactofuranoside. The ether extraction solution was distilled on a water-bath at 40–50° and the residue crystallized spontaneously.

The crystalline material was recrystallized from 30 cc. of dry ethyl acetate, when a crop of 2.8 g., with specific rotation −96° in water solution, was obtained. On further crystallization from 30 cc. of ethyl acetate, a crop of 1.00 g. of needle-like crystals was obtained, whose rotation did

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[2] Green and Pacsu, THIS JOURNAL, **59**, 1205 (1937).

[3] Green and Pacsu, *ibid.*, **59**, 2569 (1937).

[4] The authors are indebted to Miss Edna Montgomery and Dr. C. S. Hudson for the seed crystals of α-methyl-*d*-arabinofuranoside.

[5] (a) Schneider and Sepp, *Ber.*, **49**, 2054 (1916); (b) Schneider, Sepp and Stiehler, *ibid.*, **51**, 220 (1918); (c) Schneider, Gille and Eisfeld, *ibid.*, **61**, 1244 (1928).

TABLE I

Substance	Mol. wt.	M. p., °C.	$[\alpha]^{20}_D$ in H_2O	Mol. rot. in H_2O	A_x	$B_{(1-4)}$	$[\alpha]^{20}_D$ calcd.
β-Methylgalactofuranoside	194	63–65	−108	−20,950	19,110	−1150	−104.4
β-Propylgalactofuranoside	222	89–90	−100	−22,200	20,710	−1150	− 98.5
β-Benzylgalactofuranoside	270	80–81	− 96	−25,920	25,800	−1150	− 99.0
α-Methylarabinofuranoside	164	...	−125	−20,500	−18,810	−1360	−123.0
α-Ethylarabinofuranoside	178	48–49	−116	−20,650	−19,830	−1360	−119.0

not change on further recrystallization: yield of pure material 23%; m. p. 89–90°; $[\alpha]^{20}_D$ −100° (0.0500 g. substance, 3 cc. of water solution, 2-dm. semi-micro tube, rotation 3.32° to the left). The crystals did not reduce Fehling's solution and were fairly hygroscopic.

Anal. Calcd. for $C_9H_{18}O_6$: C, 48.7; H, 8.1. Found: C, 48.9; H, 7.9.

Preparation of β-Benzylgalactofuranoside.—A mixture of 5.7 g. of galactose ethylmercaptal, 10.9 g. of mercuric chloride (2 moles), 5 g. of yellow mercuric oxide, and 3 g. of drierite was shaken with 60 cc. of benzyl alcohol for ten hours at room temperature. The mixture was filtered and the filtrate diluted with 480 cc. of petroleum ether (b. p. 30–60°) and 120 cc. of benzene, then extracted[6] with four 60-cc. portions of water. The bulk of the mercuric chloride precipitated at this stage in the separatory funnel and was filtered off. The water solutions were combined, filtered, extracted with a little ether to remove any benzyl alcohol, and finally treated with 1 cc. of pyridine. A small amount of pyridine–mercuric chloride was filtered off, the solution neutralized with a few drops of sodium hydroxide solution to phenolphthalein, and evaporated *in vacuo* at 40° to a sirup. The latter was evaporated several times with absolute ethyl alcohol.

The sirup, rotating −40° in water solution, crystallized after five to six weeks in a desiccator at room temperature, and from a solution in 25 cc. of dry ethyl acetate 1.25 g. of crystals was obtained, rotating −70° in water solution. After three recrystallizations from ethyl acetate 0.65 g. of pure crystals was obtained: yield 12%; m. p. 80–81°; $[\alpha]^{20}_D$ −96° (0.0500 g. substance, 3 cc. of water solution, 2-dm. semi-micro tube, rotation 3.20° to the left). The crystals were very fine needles, were only faintly hygroscopic and did not reduce Fehling's solution.

Anal. Calcd. for $C_{13}H_{18}O_6$: C, 57.7; H, 6.8. Found: C, 57.7; H, 6.7.

Preparation of α-Methyl-*l*-arabinofuranoside.—A mixture of 5.1 g. of *l*-arabinose ethylmercaptal, 10.9 g. of mercuric chloride (2 moles), 5 g. of yellow mercuric oxide, and 3 g. of drierite was shaken with 60 cc. of absolute methyl alcohol for two hours at 25°. The reaction proceeded very fast and liberated some heat. The mixture was filtered and worked up as above for methylgalactofuranoside, and the sirup extracted with ether.

The sirup obtained rotated −96° in water solution and, upon seeding with a trace of crystalline α-methyl-*d*-arabinofuranoside, solidified in two days. From 25 cc. of dry ethyl acetate solution, 0.45 g. of pure crystals was deposited slowly at 0°. The rotation did not change on further recrystallization from 100 cc. of dry ether: yield 14%; m. p. not taken due to extreme hygroscopic nature of crystals; $[\alpha]^{20}_D$ −125° (0.0400 g. substance, 3 cc. of water solution, 2-dm. semi-micro tube, rotation 4.16° to the left). The crystals are extremely hygroscopic and devoid of action toward Fehling's solution.

Anal. Calcd. for $C_6H_{12}O_5$: C, 43.8; H, 7.3. Found: C, 43.7; H, 7.3.

Preparation of α-Ethyl-*l*-arabinofuranoside.—A mixture of 5.1 g. of *l*-arabinose ethylmercaptal, etc., as immediately above, was shaken for two hours with 60 cc. of absolute ethyl alcohol at 25°. The mixture was filtered, etc., and extracted with ether in the usual way. The sirup, which rotated −79° in water solution, changed into a crystalline mass after four months over phosphorus pentoxide.

The product was dissolved in 10 cc. of dry ethyl acetate and 0.9 g. of crystals was deposited at 0°. These crystals rotated −116° in water solution and further recrystallizations did not change this value; yield 24%; m. p. 48–49°; $[\alpha]^{20}_D$ −116° (0.2055 g. substance, 10 cc. of water solution, 2-dm. semi-micro tube, rotation 4.77° to the left). The crystals were very hygroscopic and did not reduce Fehling's solution.

Anal. Calcd. for $C_7H_{14}O_5$: C, 46.96; H, 7.86. Found: C, 46.9; H, 7.7.

Summary

β-Methyl-, β-propyl-, and β-benzylgalactofuranoside, and α-methyl- and α-ethyl-*l*-arabinofuranoside have been obtained in the crystalline state, by reaction of the ethyl mercaptal of the two sugars with mercuric chloride in a neutral solution of the respective alcohol. The rotations of the new compounds agree well with the values calculated from Hudson's rules of isorotation.

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[6] Purves and Hudson, THIS JOURNAL, **59**, 53 (1937).