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Aldehydo-*d*-β-galaheptose Hexaacetate[1]

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The study by Wolfrom[2] and his co-workers of the decomposition of ethyl mercaptal acetates by mercuric chloride in neutral aqueous acetone solutions has led to the isolation of a number of crystalline open chain acetates of the pentose and hexose series.

With the agreement of Dr. Wolfrom we have applied this reaction to the ethyl mercaptal acetate of *d*-β-galaheptose, and the present communication reports the experimental details involved in the isolation of the crystalline open chain form of *d*-β-galaheptose hexaacetate.

Experimental

d-β-Galaheptose Ethyl Mercaptal.—A solution of 20 g. of *d*-β-galaheptose in 40 cc. of concentrated hydrochloric acid was shaken at room temperature for one hour with 20 cc. of technical ethyl mercaptan, small pieces of ice were added to induce crystallization, and the separated mercaptal was filtered, washed with small portions of ice water and recrystallized from 2.5 parts of hot water; yield 14.2 g. (47%).

The mercaptal crystallizes in brilliant, colorless plates melting at 133° (corr.) to a clear colorless oil. In aqueous solution two separate preparations gave an $[\alpha]_D^{20}$ value of +37.8° (0.3834 g. in 25 cc. in a 2-dm. tube rotated 1.16° to the right).

Anal. Calcd. for $C_{11}H_{24}O_6S_2$: S, 20.27. Found: S, 20.26.

d-β-Galaheptose Ethyl Mercaptal Hexaacetate.—A solution of 11.9 g. of *d*-β-galaheptose ethyl mercaptal in a mixture of 50 cc. of pyridine and 50 cc. of acetic anhydride was cooled, kept in the ice box overnight, poured over crushed ice, the separated oil brought to crystallization by trituration, and the crude acetate filtered, washed with water, and recrystallized from solution in 3 parts of alcohol by addition of an equal volume of hot water; yield 20.3 g. (95.8%).

d-β-Galaheptose ethyl mercaptal hexaacetate crystallizes in colorless, glistening prisms melting at 105° (corr.) to a clear colorless oil. In chloroform solution a sample gave an $[\alpha]_D^{20}$ value of +26.6° (0.5221 g. in 25 cc. in a 2-dm. tube rotated 1.11° to the right), unchanged upon recrystallization from 2 parts of alcohol.

Anal. Calcd. for $C_{23}H_{30}O_{12}S_2$: S, 11.40. Found: S, 11.30.

Aldehydo-*d*-β-Galaheptose Hexaacetate.—To a vigorously stirred solution of 10 g. of *d*-β-galaheptose ethyl mercaptal hexaacetate in 36 cc. of acetone and 6 cc. water, containing a suspension of 20 g. of washed cadmium carbonate, a solution of 17.4 g. (3.6 moles) of mercuric chloride in 26 cc. of acetone was gradually added and the reaction mixture was stirred for 6 hours and allowed to stand overnight at room temperature. The next day it was heated at 50° for fifteen minutes, refluxed for fifteen minutes and filtered by suction into a flask containing cadmium carbonate. The filtrate was concentrated *in vacuo* at 35°, the residual syrup dried by several successive evaporations with acetone, extracted with purified chloroform, and the chloroform evaporated at room temperature by an air current, when the aldehydo acetate spontaneously crystallized. The yield was low (2.8 g.), but subsequent study revealed that the open chain acetate had a low solubility in acetone and a much higher yield was obtained by extracting the reaction product solids with chloroform; final yield 7.5 g. (91.5%).

Aldehydo-*d*-β-galaheptose hexaacetate crystallizes from acetone in brilliant small plates melting at 196° (corr.) to a clear oil. In purified chloroform it does not exhibit mutarotation, its $[\alpha]_D^{20}$ value being +39.9° (0.3448 g. in 25 cc. in a 2-dm. tube rotated 1.10° to the right), unchanged upon recrystallization from acetone. Upon allowing a chloroform solution to evaporate slowly large clear colorless prisms may be obtained.

Anal. Acetyl: 0.1339 g. consumed 17.18 cc. of 0.1 *N* NaOH. Calcd. for six acetyl groups, 17.38 cc. Calcd. for $C_{19}H_{26}O_{13}$: C, 49.33; H, 5.67. Found: C, 49.40; H, 5.91.

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Summary

Aldehydo-*d*-β-galaheptose hexaacetate has been prepared by Wolfrom's method, namely, by the action of mercuric chloride upon the ethyl mercaptal acetate of *d*-β-galaheptose.

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(2) Wolfrom, THIS JOURNAL, **51**, 2188 (1929); **52**, 2464 (1930); Wolfrom and Newlin, *ibid.*, **52**, 3619 (1930); **53**, 4379 (1931); Wolfrom and Orsino, *ibid.*, **56**, 985 (1934).