tory. The analyses reported were done by Micro-Tech Laboratories, Skokie, Illinois.

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Synthesis of Acetobromo Sugars

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Acetohalogen derivatives of sugars play an important role in synthetic carbohydrate chemistry and ease of preparation of these compounds is of considerable value. Formerly the classical procedure for preparing acetobromo sugars has involved treatment of the sugar acetate with a solution of hydrogen bromide in either glacial acetic acid or acetic anhydride.[3-5] Acetyl bromide has also been used.[6]

A simplified procedure for making acetobromoglucose has been described[7] in which the brominating agent (HBr) is generated *in situ* by adding water to a mixture of bromine and red phosphorus in glacial acetic acid.

We have been making use of a similar method except that no water was added to the brominating reagent (CH_3COBr). The reaction may be applied to either the free sugars or their acetates. Thus acetobromo derivatives have been prepared from the following: L-arabinose, D-xylose, D-glucose, β-D-glucose pentaacetate and β-cellobiose octaacetate (see Table I).

TABLE I

Compound	Yield, %	Acetobromo derivative M. p., ° C.	Acetobromo derivative $[\alpha]^{24}\text{D}$ ($CHCl_3$)	Ref.
L-Arabinose	22	137	+284°	8
D-Xylose	63.5[a]	....	....	9
D-Glucose	66	87–89	+195	10
β-D-Glucose pentaacetate	84	88–89	+198	10
β-Cellobiose octaacetate	95–100	185	+ 94	11

[a] This value is based on the yield of methyl β-D-xylopyranosine triacetate (m. p. 112–113°, $[\alpha]^{24}\text{D}$ −60° ($CHCl_3$)) derived from the acetobromo compound.

Experimental

Generation of the Brominating Reagent.—Bromine (180 g.) is added dropwise to suspension of red phosphorus (30 g.) in glacial acetic acid (300 ml.) with cooling. After the reaction is complete the mixture is filtered (glass wool) and kept in the cold room if not required for immediate use.

Preparation of Acetobromo Sugars. (a) From the Sugars, *e.g.*, **D-Glucose.**—The sugar (10 g.) was added with shaking to the brominating reagent (100 ml.), the temperature being kept at or below 40°. After 2 hours at room temperature, the reaction mixture was diluted with chloroform (100 ml.) and poured with stirring into a mixture of ice and water (200 ml.). The chloroform layer was separated and the aqueous layer extracted with chloroform. The chloroform extracts were combined, washed with water then with an aqueous solution of sodium bicarbonate and dried ($CaCl_2$). Removal of solvent *in vacuo* gave α-acetobromo-D-glucose which was crystallized from ether. More material was obtained by adding petroleum ether to the ethereal mother liquors.

(b) From the Sugar Acetates, *e.g.*, **β-D-Glucose Pentaacetate.**—The acetate (216 g.) was added in portions with shaking to the brominating reagent prepared from bromine (180 g.). After 2 hours at room temperature the reaction mixture was diluted with chloroform (300 ml.) and poured into a mixture of ice and water (800 ml.). The α-acetobromo-D-glucose was isolated as in (a).

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Synthesis of Glycol Bis-(alkyl Sulfites)[1]

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Esters of sulfurous acid of various types are known, simple esters having been prepared long ago.[2] Richter[3] obtained diaryl sulfites while Carre and Libermann[4] prepared many mixed esters, including alkyl aryl sulfites. Some cyclic esters of glycols are known[5] and also the cyclic ester of catechol.[6]

However, no mixed diesters of glycols have been reported. It was the purpose of this work to attempt to prepare mixed glycol bis-(alkyl sulfites) of the type formula: $RO\cdot SO\cdot O\cdot (CH_2)_2\cdot X\cdot (CH_2)_2\cdot O\,SO\cdot OR$ where R is ethyl or β-chloroethyl and X is oxygen or sulfur. In addition diesters of tetramethylene glycol were studied.

The compounds were employed in tumor chemotherapy tests in mice. Structures of this type possess a formal analogy to the disulfonic esters of Timmis[7] who showed that the dimethanesulfonate of tetramethylene glycol has activity in causing tumor regression.

The glycol diesters were prepared by reaction of one mole of glycol in inert solvent medium with two moles of an ester chloride of sulfurous acid (alkyl chlorosulfites) in the presence of pyridine.[8] The syntheses were successful with tetramethylene glycol, diethylene glycol, thiodiglycol and butyne diol, when reacted with ethyl or β-chloroethyl chlorosulfites. The products, after appropriate purification, were high boiling oils of little or no odor. Several of the bis-(ethyl sulfites) were distilled but no attempt was made to distil the chloroethyl esters. None of these substances is steam volatile and they did not appear to decompose during short contact with boiling water.

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