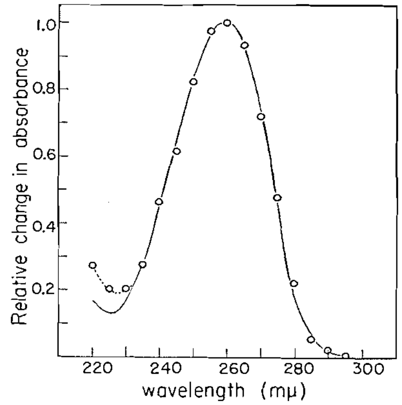

FIG. 2. Plot of $\Delta D/\Delta D_{260}$, where ΔD is the change in optical density at any wavelength and ΔD_{260} is the corresponding change at 260 mμ that occurs when the product of irradiation of uracil (solid line) or the product of the reduction of 5,5-dibromo-6-hydroxy-hydrouracil (open circles) is treated with HCl (100°, 5 minutes, pH 1). This method of presentation was chosen because the concentrations obtained in the two preparations were arbitrary.

tions, adds strong support to the suggestion made earlier (2) that the product of irradiation of uracil responsible for the acid-catalyzed regeneration phenomenon is 6-hydroxy-hydrouracil.

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AN ALTERNATIVE SYNTHESIS OF 2-*O*-METHYL-D-XYLOSE

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In studying the structure of a xylan the need arose for 2-*O*- and 3-*O*-methyl-D-xylose as reference compounds. The latter was synthesized from 1,2-*O*-isopropylidene-D-xylofuranose (1) and it was preferable to prepare the former from the same starting material if possible. Such a procedure would also obviate the necessity of using the acid-labile methyl 3,5-*O*-isopropylidene-α,β-D-xylofuranoside as described in a previous synthesis of 2-*O*-methyl-D-xylose (2).

1,2-*O*-Isopropylidene-D-xylofuranose was benzylated to give the corresponding 3,5-di-*O*-benzyl derivative, which was converted to methyl 3,5-di-*O*-benzyl-α,β-D-xylofuranoside by methanolysis. Methylation (3) of this compound yielded the 2-*O*-methyl derivative, which was then reductively debenzylated to methyl 2-*O*-methyl-α,β-D-xylofuranoside. Hydrolysis of this compound gave crystalline 2-*O*-methyl-D-xylose.

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EXPERIMENTAL

*3,5-Di-O-benzyl-1,2-O-isopropylidene-*D*-xylofuranose*

1,2-*O*-Isopropylidene-D-xylofuranose, $[\alpha]_D^{21}$ −19.2° (*c*, 2.1 in water), (46.4 g.) (1) was treated with benzyl chloride (230 ml.) and powdered potassium hydroxide (57 g.) at 100° C. for 5 hours. The solution was poured into water and the sirupy material obtained on concentration was extracted with boiling ethanol. Evaporation yielded a sirup (103.2 g.) which could not be induced to crystallize, $[\alpha]_D^{22}$ +9.2° (*c*, 2.5 in ethanol). Anal.: Calc. for $C_{22}H_{26}O_5$: C, 71.3%; H, 7.1%. Found: C, 72.3%; H, 7.5%.

*Methyl 3,5-Di-O-benzyl-α,β-*D*-xylofuranoside*

A portion of the above sirup (40.0 g.) was boiled under reflux with anhydrous methanol (200 ml.) containing 1.5% hydrogen chloride. Neutralization (silver carbonate) and evaporation yielded a sirup, $[\alpha]_D^{22}$ +17.6° (*c*, 5.3 in ethanol), (37.5 g., 100.8%). Anal.: Calc. for $C_{20}H_{24}O_5$: OCH_3, 9.0%. Found: OCH_3, 8.8%.

*Methyl 3,5-Di-O-benzyl-2-O-methyl-α,β-*D*-xylofuranoside*

The above sirupy compound (37.0 g.) was dissolved in a mixture of dimethyl formamide (54 ml.) and methyl iodide (20.4 ml.). Silver oxide (20.4 g.) was added in small portions over a period of 1 hour and the mixture was shaken for 24 hours. The methylated material was recovered (3) to yield a sirup, $[\alpha]_D^{22}$ +23.7° (*c*, 3.2 in ethanol), (33.3 g., 86.5%). Anal.: Calc. for $C_{21}H_{26}O_5$: C, 70.4%; H, 7.3%; OCH_3, 17.3%. Found: C, 71.5%; H, 8.1%; OCH_3, 17.6%. An infrared spectrum of the material indicated the presence of only a trace of hydroxyl groups.

*Methyl 2-O-Methyl-α,β-*D*-xylofuranoside*

The above sirup (33.0 g.) was reductively debenzylated (4). The aqueous solution obtained was passed through a column of Amberlite IRC 50 exchange resin and the eluate was concentrated and extracted with ethanol to yield a sirup, $[\alpha]_D^{22}$ +35.4° (*c*, 2.9 in ethanol), (22.1 g.).

*2-O-Methyl-*D*-xylose*

The above material (22.0 g.) was hydrolyzed with 0.5 *N* sulphuric acid (150 ml.) by boiling under reflux for 14 hours. After neutralization with barium hydroxide and filtration through Celite, concentration of the filtrate gave a sirup (7.5 g.). Examination by paper chromatography using a system of methyl ethyl ketone – ethanol – water (20:5:2) indicated the presence of 2-*O*-methyl-D-xylose and a trace of xylose.

The crude material was added to the top of a column containing cocoanut charcoal and was eluted with 2% ethanol until the eluate gave a negative Molisch test. Evaporation yielded a white, crystalline compound, which was recrystallized from ethanol, m.p. 132–133° C. (corrected), $[\alpha]_D^{21}$ +35.1° (*c*, 3.5 in water), (3.1 g., 15.3%). Anal.: Calc. for $C_6H_{12}O_5$: OCH_3, 18.9%. Found: OCH_3, 18.9%.

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