the *Acetobacter* dextran with concanavalin reagent. Thus, while the dextrans formed by *Leuconostoc mesenteroides* and *Streptococcus* group H, show no significant reaction with concanavalin, the polysaccharide formed by *Acetobacter capsulatum* shows a glycogen-value equivalent to 60% of that shown by normal human liver glycogen (see Table I).

Fractionation of the polyglucosan synthesized by *Acetobacter capsulatum* on a limited scale gave two fractions, one of which showed a small increase in the glycogen value (Table II). Unlike the *Neisseria* polysaccharide which gave rise to fractions that became less opalescent in aqueous solution as the glycogen value increased, the *Acetobacter* polysaccharide fraction which formed the more opalescent solution showed the larger glycogen value.

The above results indicate that the *Acetobacter* polysaccharide must differ in some respect from the other dextrans tested. The nature of this difference has yet to be ascertained. That the results may be due to the presence of glycogen-like material is possible but unlikely since periodate oxidation, in which the periodate consumption was 1.89 moles per anhydroglucose unit,[18] resulted in the formation of 0.82 mole of formic acid per anhydroglucose unit. Such results favor a dextran type of structure for the *Acetobacter* polyglucosan in which the ratio of 1,6-linkages to other types is 5:1. It is conceivable that the difference between the *Leuconostoc* dextran and the *Acetobacter* polyglucosan is due to the presence of linkages in the latter which are not of the 1,6-type. The formation of dextrans with varying types of linkages[19] may make it possible to test this hypothesis and information bearing on this point is now being sought.

(19) J. C. Rankin and A. Jeanes, THIS JOURNAL, **76**, 4435 (1954).

Reports on the isolation of glycogen-like substances from bacteria other than *Neisseria* have been few. Glycogens have been isolated from avian tubercle bacilli,[20] from *Bacillus megatherium*[21] and most recently from enteric bacteria.[22]

Glycogens from *Aerobacter aerogenes* and *Salmonella montevideo* (enteric bacteria) grown on nutrient agar containing 1% mannose for the *Salmonella* and 1% glucose for the *Aerobacter* cultures were examined by means of the concanavalin–polysaccharide reaction. The results which are shown in Table I indicate that the bacteria produced glycogens of the normal type, although the *Salmonella* glycogen gave a somewhat higher than average glycogen-value.

Treatment of the three preparations from the enteric bacteria with diluted saliva resulted in their rapid degradation to the point where they no longer reacted visibly with concanavalin reagent. It was interesting, however, that the *Salmonella* glycogen which was slightly impure as obtained from Dr. Levine was not degraded by β-amylase until it was further purified. All three of the purified glycogens underwent a 30–40% hydrolysis when treated with β-amylase, a result in agreement with the values shown by most animal glycogens.

Acknowledgment.—The authors thank Dr. E. J. Hehre for the samples of *Neisseria*, *Acetobacter* and *Streptococcal* dextrans, Dr. Allene Jeanes for the *Leuconostoc* dextran and Dr. Seymour Levine for the enteric bacterial glycogens.

(20) E. Chargaff and D. H. Moore, *J. Biol. Chem.*, **155**, 493 (1944).

(21) C. Barry, R. Gavard, C. Milhaud and J. P. Aubert, *Compt. rend.*, **235**, 1062 (1952).

(22) S. Levine, H. J. R. Stevenson, E. C. Tabor, R. H. Bordner and L. A. Chambers, *J. Bact.*, **66**, 664 (1953).

ST. PAUL 1, MINNESOTA

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL BIOCHEMISTRY, COLLEGE OF AGRICULTURE, UNIVERSITY OF CALIFORNIA]

Anomeric 1-Dicyclohexylammonium Phosphate Esters of D-Glucopyranose, D-Galactopyranose, D-Xylopyranose and L-Arabinopyranose[1]

BY E. W. PUTMAN AND W. Z. HASSID

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Three new phosphorylated pentose derivatives, β-D-xylose 1-phosphate and the α- and β-forms of L-arabinose 1-phosphate have been obtained as crystalline cyclohexylammonium salts. In addition the cyclohexylammonium salts of the 1-phosphoric acid esters of α-D-xylose, α- and β-D-glucose and α- and β-D-galactose have been prepared. The cyclohexylammonium salts of these phosphorylated sugars may be purified readily by recrystallization, in contrast to the barium salts which are amorphous and usually contain anomeric impurities. Application of Hudson's isorotation rules to the α- and β-anomers of the four phosphorylated sugars shows the 2A values to be consistent with the first isorotation rule, the average value being 25,400. However, the 2B values are greater than those of the corresponding methyl glycosides by about 9,000 molecular rotation units.

Previous investigations revealed that mung bean seedlings contain uridyl pyrophosphorylases capable of catalyzing the reversible formation of uridine diphosphate D-glucose from uridine triphosphate and α-D-glucose 1-phosphate, as well as the formation of uridine diphosphate D-xylose from uridine triphosphate and α-D-xylose 1-phosphate.[2] For continuation of these studies pure α- and β-forms of 1-phosphate esters of D-galactose, D-glucose, D-xylose and L-arabinose were required.

(1) This work was supported in part by a research contract with the United States Atomic Energy Commission.

(2) V. Ginsburg, E. F. Neufeld and W. Z. Hassid, *Proc. Natl. Acad. Sci. U. S.*, **42**, 333 (1956).

Of these phosphorylated sugars, only the α-forms of D-glucose 1-phosphate,[3] D-galactose 1-phosphate,[4] and D-xylose 1-phosphate[5] have been prepared as crystalline potassium salts free of impurities. β-D-Galactose 1-phosphate and β-D-glucose 1-phosphate have been reported as amorphous barium salts,[6] the latter also as a crystalline brucine salt.[7] The 1-phosphate esters of β-D-xylose, β-L-arabinose and α-L-arabinose have not been previously described.

The aldose 1-phosphates are readily synthesized from the fully acetylated aldopyranosyl 1-bromo derivatives by a halogen replacement reaction employing silver salts. In this series of configurationally related sugars (glucose series as opposed to that of mannose), treatment with trisilver phosphate[8] followed by acid hydrolysis of the resultant triglycosyl phosphate ester yields predominantly the 1,2-*cis*-monoester, in which the configuration of the glycosidic carbon and of the pyranose ring is preserved. A similar result may be obtained by the reaction between the acetylated 1-bromo sugar and silver diphenylphosphate, followed by hydrogenolysis of the phenyl groups.[8]

When the bromine is replaced by phosphate using monosilver phosphate, by the method of Reithel,[6] the ring configuration is maintained in the phosphorylated sugar but an inversion occurs at C-1 resulting in the 1,2-*trans*-glycosyl ester as the principal product. The 1,2-*trans*-monoesters also result from the reaction with silver dibenzylphosphate and subsequent hydrogenolysis.[7]

All these methods produce crude glycosyl phosphates which are isolated as amorphous barium salts by alcohol precipitation from aqueous solutions after deacetylation. Some degree of purification may be achieved by repeated solution in water and reprecipitation with alcohol; however, this procedure fails to remove anomeric impurities.

Within recent years cyclohexylamine has been successfully employed for the preparation of crystalline salts of phosphorylated sugars. As a result, deoxyribose 1-phosphate[9] and D-fructose 1,6-diphosphate[10] were obtained readily as crystalline cyclohexylammonium salts by the use of this reagent. A number of other phosphorylated carbohydrates also have been crystallized as pure cyclohexylammonium salts by various investigators.[11]

(3) C. F. Cori, S. P. Colowick and G. T. Cori, *J. Biol. Chem.*, **121**, 465 (1937).

(4) H. W. Kosterlitz, *Biochem. J.*, **33**, 1087 (1939).

(5) W. R. Meagher and W. Z. Hassid, THIS JOURNAL, **68**, 2135 (1946).

(6) F. J. Reithel, *ibid.*, **67**, 1056 (1945).

(7) M. L. Wolfrom, C. S. Smith, D. E. Pletcher and A. E. Brown, *ibid.*, **64**, 23 (1942).

(8) T. Posternak, *ibid.*, **72**, 4824 (1950).

(9) M. Friedkin, *J. Biol. Chem.*, **184**, 449 (1950). According to this author the use of cyclohexylamine as a reagent for the preparation of crystalline sugar phosphate esters was suggested by Malcom Clark of Cambridge.

(10) R. J. McGilvary, *ibid.*, **200**, 835 (1953). This author points out the advantage of cyclohexylamine as compared with alkaloids for the preparation of crystalline salts of phosphate esters to be used in biological systems.

(11) J. G. Moffatt and H. G. Khorana, THIS JOURNAL, **78**, 883 (1956); G. M. Tener, R. S. Wright and H. G. Khorana, *ibid.*, **78**, 506 (1956); C. E. Ballou and H. O. L. Fischer, *ibid.*, **78**, 1695 (1956); D. L. MacDonald, H. O. L. Fischer and C. E. Ballou, *ibid.*, **78**, 3720 (1956).

The present paper describes three new phosphorylated pentose derivatives, namely, the α- and β-anomers of L-arabinose 1-phosphate and the β-anomer of D-xylose 1-phosphate as cyclohexylammonium salts. In addition, α-D-xylose 1-phosphate and the α- and β-forms of D-glucose 1-phosphate and of D-galactose 1-phosphate were prepared as the crystalline dicyclohexylamine salts.

The empirical formulas and molecular weights assigned to these compounds were calculated from the results of elementary analyses for carbon, hydrogen, nitrogen and phosphorus. The salts of both β-D-glucose 1-phosphate and β-D-galactose 1-phosphate are hydrated and crystallize in the form of dense short thick needles. The other salts are anhydrous and crystallize as fine light and fluffy needles.

The salts of these phosphorylated sugars melt with decomposition. The range of melting was determined by heating the compounds rapidly to a temperature below decomposition and then increasing the temperature 2° per minute. The first figures in Table I, column 2, indicate the initiation of browning; the second figures give the temperatures at which complete decomposition takes place. The rotations of the phosphorylated sugars were made in aqueous solutions, *p*H 7.8, at a concentration of 2.5%.

TABLE I

PROPERTIES OF THE DICYCLOHEXYLAMMONIUM SALTS OF FOUR PAIRS OF ANOMERS OF ALDOSE 1-PHOSPHORIC ACID ESTERS

Aldose component	Molecular weight	M.p., °C.	$[\alpha]^{26}D$ (*c* 2.5, in water at *p*H 7.8)
α-D-Glucopyranose	458	163–169	+64.0°
β-D-Glucopyranose·$C_2H_5OH·H_2O$	522	137–143	+ 7.3
α-D-Xylopyranose	428	152–158	+58.0
β-D-Xylopyranose	428	144–150	+ 0.8
α-D-Galactopyranose	458	147–153	+78.5
β-D-Galactopyranose·H_2O	476	145–151	+21.0
β-L-Arabinopyranose	428	155–161	+91.0
α-L-Arabinopyranose	428	144–150	+30.8

The possibility of anomeric contamination in these derivatives could not be entirely excluded, except in the case of β-glucose 1-phosphate. The crude dicyclohexylammonium salt of this compound gave a positive amylose test after incubation with potato phosphorylase, showing contamination with the α-anomer.[12] However, after three recrystallizations from 95% ethanol the extent of contamination was reduced to less than 0.1% as shown by enzymatic assay.[13] Since methods for the estimation of purity of the other phosphorylated sugars are not readily available, they were subjected to three recrystallizations, and it was then assumed that their state of purity was comparable to that of the β-D-glucose 1-phosphate.

The values for the molecular rotations of the cyclohexylamine salts of the 1-phosphoric acid esters of α-D-glucose, α-D-xylose and α-D-galactose agree with the recorded values found in the litera-

(12) W. Z. Hassid and R. M. McCready, *ibid.*, **63**, 2171 (1941)

(13) A. Munch-Petersen, H. M. Kalckar, E. Cutolo and E. E. B. Smith, *Nature*, **172**, 1036 (1953).

TABLE II

COMPARISON OF THE MOLECULAR ROTATIONS OF THE ANOMERIC 1-PHOSPHATE ESTERS WITH THE RELATED METHYL ALDOPYRANOSIDES

Aldose component	Phosphate esters $[M]^{25}D$	2A	2B	Methyl pyranosides $[M]D$	2A'	2B'
α-D-Glucopyranose	29,300	25,500	33,100	30,900	37,600	24.200
β-D-Glucopyranose	3,800			−6,700		
α-D-Xylopyranose	24,800	24,500	25,100	25,300	36,100	14,500
β-D-Xylopyranose	300			−10,800		
α-D-Galactopyranose	36,000	26,000	46,000	38,000	38,000	38,000
β-D-Galactopyranose	10,000			0		
β-L-Arabinopyranose	39,000	25,800	52,200	40,000	37,100	43,100
α-L-Arabinopyranose	13,200			2,900		

ture.[3-5] There appears to be little variation in the observed molecular rotations whether the phosphorylated sugar is in the form of potassium salt, barium salt or free acid. However, when the rotations of the β-anomers were measured in 0.5 *N* hydrochloric acid, the values were about 4,000 rotational units lower than the values obtained at *p*H 7.8. No rotational data for crystalline derivatives of the other phosphorylated sugars listed in Tables I and II that could be compared with those of the cyclohexylamine derivatives are reported in the literature.

Because of the structural similarities of these four sugars, differing only in the configuration at carbon 4 and substitution at carbon 5, the anomeric differences in their molecular rotation, 2A, should, according to Hudson's first rule of isorotation,[14] be of the same order of magnitude. For the purpose of comparison, rotational data for the related methyl glycosides have been included in Table II.[15] There is a good agreement of the 2A values in the phosphate ester series, and variations from the average value of 25,400 are of the same order of magnitude as the variations in the series of related methyl glycosides (average 2A' value, 37,200).

The values 2B and 2B' represent the sums of the molecular rotations of the anomeric pairs which in accordance with the second rule of isorotation should be approximately the same for derivatives possessing identical ring configurations. In all cases the 2B values for the phosphate esters are higher than those of the methyl glycosides, 2B', by about 9,000 molecular rotation units.

The rotations of the 1,2-*cis* anomers in the ester series are lower than the related methyl pyranosides by an average value of 1,300, whereas the 1,2-*trans*-esters have molecular rotations that average 10,500 units higher than the methyl pyranosides. Thus the major deviations from the second rule of isorotation in the 1-phosphate ester series of the sugars is manifested by the increased rotation of the 1,2-*trans* anomers.

Experimental

Preparation of β-D-Glucose 1-Phosphate, β-D-Galactose 1-Phosphate, β-D-Xylose 1-Phosphate and α-L-Arabinose 1-Phosphate as the Barium Salts.—These hexose phosphates were prepared by the method of Reithel.[6] The starting materials were 0.15 *M* quantities of 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide, 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranosyl bromide, 2,3,4-tri-*O*-acetyl-α-D-xylopyranosyl bromide and 2,3,4-tri-*O*-acetyl-β-L-arabinopyranosyl bromide. These acetobromo sugars in chloroform solution were treated with 0.15 *M* quantities of monosilver phosphate for 15 minutes at 5° and the products isolated as the barium salts. The acetylated phosphate esters were then deacetylated in absolute ethanol with catalytic amounts of sodium methoxide.

The barium salts were partially purified by repeated solution in water and reprecipitation with 1.5 volumes of ethanol until the ratio of the reducing sugar to inorganic phosphate after ten minutes hydrolysis with 1 *N* hydrochloric acid was unity. The final yields of the amorphous barium salts which met this criterion were approximately 7.5 g. of the hexose esters, and 6.5 g. of the pentose esters.

Preparation of the Barium Salts of 1-Phosphoric Acid Esters of α-D-Glucose, α-D-Galactose, α-D-Xylose and β-L-Arabinose.—The method of Cori, Colowick and Cori[3] was used for the preparation of the barium salts of the phosphoric acid esters. The starting materials were 0.15 *M* quantities of the corresponding acetobromo sugars which were refluxed for one hour in benzene with 0.05 *M* trisilver phosphate. The reaction products, acetylated triglycosyl phosphate esters, were isolated by precipitation with petroleum ether and partially hydrolyzed and deacetylated with methanolic HCl to yield the monoesters. The phosphorylated sugars were isolated as the barium salts as previously described. The yields of the salts were approximately 10% of the theoretical, based on the acetobromo sugars.

Conversion of the Barium Salts of the Phosphorylated Sugars into the Cyclohexylammonium Salts.—A 1.5-g. sample of each of the barium salt preparations was dissolved in 15 ml. of water and passed through a small column of Dowex 50 to adsorb the barium. The effluent was neutralized with 0.5 *M* alcoholic solution of cyclohexylamine and evaporated to dryness by vacuum distillation.

All of these compounds crystallized as the cyclohexylammonium salts during concentration of the solutions, except that of the β-D-galactose 1-phosphate preparation. Preliminary attempts to crystallize the latter as a cyclohexylammonium salt were not successful, until the crude ester had been first partially purified as the brucine salt.

A 3-g. β-D-galactose 1-(barium phosphate) sample (5.7 m*M* on the basis of phosphorus content) was passed through a Dowex 50 column to remove the barium, and the resultant acidic solution treated with 14 m*M* brucine in ethanol. After extraction of the excess brucine with chloroform and evaporation of the aqueous solution, a crystalline product, presumably the dibrucine salt of β-D-galactose 1-phosphate, was obtained. The yield was 5 g. (70% on the basis of the barium salt). The product was twice recrystallized from 80% ethanol and then treated in aqueous solution with an excess of barium hydroxide. The precipitated brucine was extracted with chloroform, followed by addition of two volumes of ethanol to the aqueous phase to precipitate the barium salt of the β-D-galactose 1-phosphate. When this salt was dissolved in water and reprecipitated from ethanol, 1.1 g. of the barium salt was recovered. The product, after conversion to the free acid, was neutralized with an alcoholic solution of cyclohexylamine and concentrated to a sirup. When the sirup was taken up in boiling ethanol and allowed to cool, the cyclohexylammonium salt separated out in crystalline form.

The crude amine salts of the various ester preparations

(14) C. S. Hudson, THIS JOURNAL, **31**, 66 (1909).

(15) F. J. Bates and associates, "Polarimetry, Saccharimetry and the Sugars," U. S. Department of Commerce, Circular C440, U. S. Government Printing Office, Washington, D. C., 1942, Table 148, pp. 708, *et seq.*

were collected by filtration, washed with ethanol, and air-dried. The compounds were purified as follows: The dry salts were dissolved in water, treated with Darco G-60, filtered and concentrated in a vacuum desiccator. The pentose phosphates, all of which crystallized during concentration of their aqueous solutions, were recrystallized from 80% ethanol. The sirups of the hexosephosphates which did not crystallize from aqueous solution were taken up in a minimum amount of boiling 95% ethanol. Crystallization occurred as the solutions cooled to room temperature in a desiccator.

At this stage of purification the β-D-glucose 1-phosphate prepration still gave a positive qualitative test for α-D-glucose 1-phosphate when tested with potato phosphorylase.[12] Accordingly, all eight of the sugar phosphate preparations were subjected to two additional recrystallizations by the procedure previously described.

The thrice-recrystallized β-D-glucose 1-phosphate preparation gave an inconclusive test for α-anomer contamination when it was treated with potato phosphorylase. The limit of contamination was therefore estimated by an enzymatic assay in which the α-D-glucose 1-phosphate was converted to D-glucose 6-phosphate and determined spectrophotometrically by measuring the reduction of triphosphopyridine nucleotide concomitant with the oxidation of D-glucose 6-phosphate to 6-phospho-D-gluconic acid catalyzed by D-glucose 6-phosphate dehydrogenase.[13]

The reaction mixture consisted of 3 μM of dicyclohexylammonium β-D-glucopyranosylphosphoric acid (0.03 ml. of a 0.10 M solution), 0.05 ml. of a 2% solution of D-glucose 6-phosphate dehydrogenase, 0.05 ml. of a 0.1% solution of crystalline phosphoglucomutase, 0.03 ml. of 0.1 M $MgCl_2$, 0.10 ml. of a 0.5% solution of triphosphopyridine nucleotide and 0.8 ml. of 0.1 M Tris buffer, pH 7.5. During the first 6 minutes incubation at 25° the digest showed an increase in optical density at 340 mμ of 0.01 optical density unit. No further change was observed in an ensuing period of 27 minutes. Since 0.01 μM of authentic α-D-glucose 1-phosphate caused an increase in O.D. at 340 mμ of 0.06 unit by this assay method, no more than 0.0017 μM of α-D-glucose 1-phosphate was shown to be present in the 3.0 μM sample of β-D-glucose 1-phosphate. It was therefore assumed that anomeric contamination of the other preparations had been reduced to an equally low level of the order of 0.1% or less.

The cyclohexylammonium phosphate esters were dried in air at room temperature and submitted for chemical analysis.

Analytical Results

α-D-**Glucopyranosyl 1-(dicyclohexylammonium phosphate**): *Anal.* Calcd. for $C_6H_{13}O_9P(C_6H_{11}NH_2)_2$: C, 47.20; H, 8.58; N, 6.12; P, 6.77. Found: C, 47.03; H, 8.49; N, 5.83; P, 6.82.

β-D-**Glucopyranosyl 1-(dicyclohexylammonium phosphate**): *Anal.* Calcd. for $C_6H_{13}O_9P(C_6H_{11}NH_2)_2C_2H_5OH\cdot H_2O$: C, 46.00; H, 9.06; N, 5.35; P, 5.92. Found: C, 45.88; H, 8.84; N, 4.98; P, 5.91.

α-D-**Xylopyranosyl 1-(dicyclohexylammonium phosphate**): *Anal.* Calcd. for $C_5H_{11}O_8P(C_6H_{11}NH_2)_2$: C, 47.70; H, 8.72; N, 6.54; P, 7.23. Found: C, 47.32; H, 8.16; N, 6.55; P, 7.27.

β-D-**Xylopyranosyl 1-(dicyclohexylammonium phosphate**): *Anal.* Calcd. for $C_5H_{11}O_8P(C_6H_{11}NH_2)_2$: C, 47.70; H, 8.72; N, 6.54; P, 7.23. Found: C, 46.45; H, 8.39; N, 6.60; P, 7.12.

α-D-**Galactopyranosyl 1-(dicyclohexylammonium phosphate**): *Anal.* Calcd. for $C_6H_{13}O_9P(C_6H_{11}NH_2)_2$: C, 42.20; H, 8.58; N, 6.12; P, 6.77. Found: C, 47.35; H, 8.49; N, 5.96; P, 6.79.

β-D-**Galactopyranosyl 1-(dicyclohexylammonium phosphate**): *Anal.* Calcd. for $C_6H_{13}O_9P(C_6H_{11}NH_2)_2\cdot H_2O$: C, 45.30; H, 8.69; N, 5.88; P, 6.52. Found: C, 44.94; H, 8.44; N, 6.04; P, 6.66.

α-L-**Arabinopyranosyl (1-dicyclohexylammonium phosphate**): *Anal.* Calcd. for $C_5H_{11}O_8P(C_6H_{11}NH_2)_2$: C, 47.70; H, 8.72; N, 6.54; P, 7.23. Found: C, 47.35; H, 8.63; N, 6.62; P, 7.14.

β-L-**Arabinopyranosyl (1-dicyclohexylammonium phosphate**): *Anal.* Calcd. for $C_5H_{11}O_8P(C_6H_{11}NH_2)_2$: C, 47.70; H, 8.72; N, 6.54; P, 7.23. Found: C, 47.81; H, 8.80; N, 6.64; P, 7.09.

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[CONTRIBUTION FROM THE LABORATORIES OF THE SLOAN-KETTERING DIVISION, CORNELL UNIVERSITY MEDICAL COLLEGE]

Pyrimidine Nucleosides. III. On the Syntheses of Cytidine and Related Pyrimidine Nucleosides[1]

BY JACK J. FOX, NAISHUN YUNG, IRIS WEMPEN AND IRIS L. DOERR

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Procedures are described for the synthesis of cytidine (and thus of uridine) by condensation of mercury derivatives of certain pyrimidines with tri-*O*-benzoyl-D-ribofuranosyl halides. The synthesis of 1-β-D-xylofuranosylcytosine is also described.

Metabolic studies have shown that, with the mammal, exogenously supplied uracil, thymine and cytosine are not extensively incorporated into polynucleotides; whereas cytidine, and to a lesser extent uridine and thymidine, is extensively incorporated into pentose and deoxypentose nucleic acids.[2] These studies point to the desirability of developing, for the synthesis of cytidine, methods adaptable for the incorporation of radioisotopes and for the synthesis of analogs of cytidine for study as potential chemotherapeutic agents or as metabolite antagonists.

Howard, *et al.*,[3] synthesized cytidine by the Hilbert–Jansen procedure[4] by the condensation of 2,4-diethoxypyrimidine with tri-*O*-acetyl-D-ribofuranosyl bromide. The yields, however, were quite low (0.35 g. of cytidine sulfate from 15 g. of the pyrimidine and 5 g. of halogenose). In part I of this series[5] it was shown that thymine nucleosides may be prepared in good yields *via* the condensation of a mercury derivative of thymine with poly-*O*-acylglycopyranosyl *or* poly-*O*-acylglycofuranosyl

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(2) See chapter by G. B. Brown and P. M. Roll in E. Chargaff and J. N. Davidson, "The Nucleic Acids," Vol. II, Academic Press, Inc., New York, N. Y., 1951, p. 341, for a comprehensive review of these studies.

(3) G. A. Howard, B. Lythgoe and A. R. Todd, *J. Chem. Soc.*, 1052 (1947).

(4) G. E. Hilbert and E. F. Jansen, THIS JOURNAL, **58**, 60 (1936).

(5) J. J. Fox, N. Yung, J. Davoll and G. B. Brown, *ibid.*, **78**, 2117 (1956).