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SYNTHESIS OF 2,3-UNSATURATED POLYSACCHARIDES FROM AMYLOSE AND XYLAN*†

DEREK HORTON AND MAKRAM H. MESHREKI
Department of Chemistry, The Ohio State University, Columbus, Ohio 43210 (U. S. A.)
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ABSTRACT

Amylose (**1**) was tritylated at O-6, the ether *p*-toluenesulfonylated at O-2 and O-3, and the product (**3**) treated with sodium iodide and zinc dust in *N*,*N*-dimethylformamide, to give 2,3-dideoxy-6-*O*-trityl-α-D-*erythro*-hex-2-enopyranoglycan (**4**). This 2,3-unsaturated polysaccharide could be converted into a 2,3-dibromo derivative (**5**), and hydrogenated with concomitant detritylation to the saturated analogue (**6**), and, on treatment with aqueous acetic acid, it gave 2-(D-*glycero*-1,2-dihydroxyethyl)-furan (**8**). The 2,3-bis(*p*-toluenesulfonate) (**10**) of β-D-xylan (**9**) was similarly converted into the 2,3-unsaturated polysaccharide, 2,3-dideoxy-β-D-*glycero*-pent-2-enopyranoglycan (**11**), which, with aqueous acetic acid, gave 2-(hydroxymethyl)furan (**12a**).

INTRODUCTION

Earlier papers in this series have described[4,5] preparative procedures for introducing alkene-type unsaturation into derivatives of simple sugars, and it has been shown[4,6] that the 2,3-unsaturated D-hexosides react extremely readily with acid to give 2-(D-*glycero*-1,2-dihydroxyethyl)furan. This work has comprised part of a broader program directed toward the application of the reactions to starch and related polysaccharides. In contrast to the wealth of literature on *O*-substituted derivatives of polysaccharides, few studies have been made on deoxygenated or C=C unsaturated derivatives, although such derivatives of abundant polysaccharides might offer useful routes of access to simple organic molecules, as well as providing polymers of novel functionality and potential utility. As organic raw materials, such ubiquitous and continually replenished polysaccharides as starch and cellulose could complement technology based on dwindling reserves of fossil fuels, if suitable procedures for decreasing the level of oxygenation in the polysaccharides could be devised.

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This paper describes the deoxygenation of amylose, the linear component of starch, to the corresponding polymeric 2,3-alkene, together with studies on reactions of the double bond in the polymer and on the acid-catalyzed degradation of this unsaturated polyacetal. As a simpler model for this reaction, a (1→4)-β-D-pentoglycan (β-D-xylan) has likewise been converted into its 2,3-unsaturated analogue, and this product has been characterized by degradation.

DISCUSSION

Amylose (**1**) was tritylated with chlorotriphenylmethane in pyridine to give a quantitative yield of 6-*O*-tritylamylose[7,8] (**2**), having a degree of substitution (d.s.) of 1.0, as a pyridine-soluble, methanol-insoluble, white powder. *p*-Toluenesulfonylation of this product with an excess of *p*-toluenesulfonyl chloride in pyridine gave 2,3-di-*O*-*p*-tolylsulfonyl-6-*O*-tritylamylose (**3a**) of[9] d.s. 1.0 by trityl and 1.8 by *p*-tolylsulfonyl in quantitative yield; the product contained no chlorine, and its n.m.r. spectrum in pyridine-d_5 showed resonances having the anticipated intensities for the structure indicated (see Experimental section). The corresponding 2,3-bis(methanesulfonate) (**3b**) was prepared similarly from **2**; complete substitution (d.s. 2.0 by methylsulfonyl) was achieved under conditions considerably milder than those required for *p*-toluenesulfonylation.

The 2,3-bis(*p*-toluenesulfonate) **3a** was converted into the 2,3-unsaturated polymer **4** by the action of[4,5,10] an excess of sodium iodide and zinc dust in *N*,*N*-dimethylformamide for 6–12 h at 180–200°. The product was isolated, in ~60% yield after dialysis, as a pale-brownish powder whose n.m.r. spectrum showed that all *p*-tolylsulfonyloxyl groups had been removed, as aryl *C*-methyl signals were absent. Analysis for the trityl group[8] indicated that the product still had d.s. 1.0 by the trityl group, and sulfur was absent. The elemental composition accorded[9] with the formula **4** having d.s. 0.75 by the double bond between C-2 and C-3.

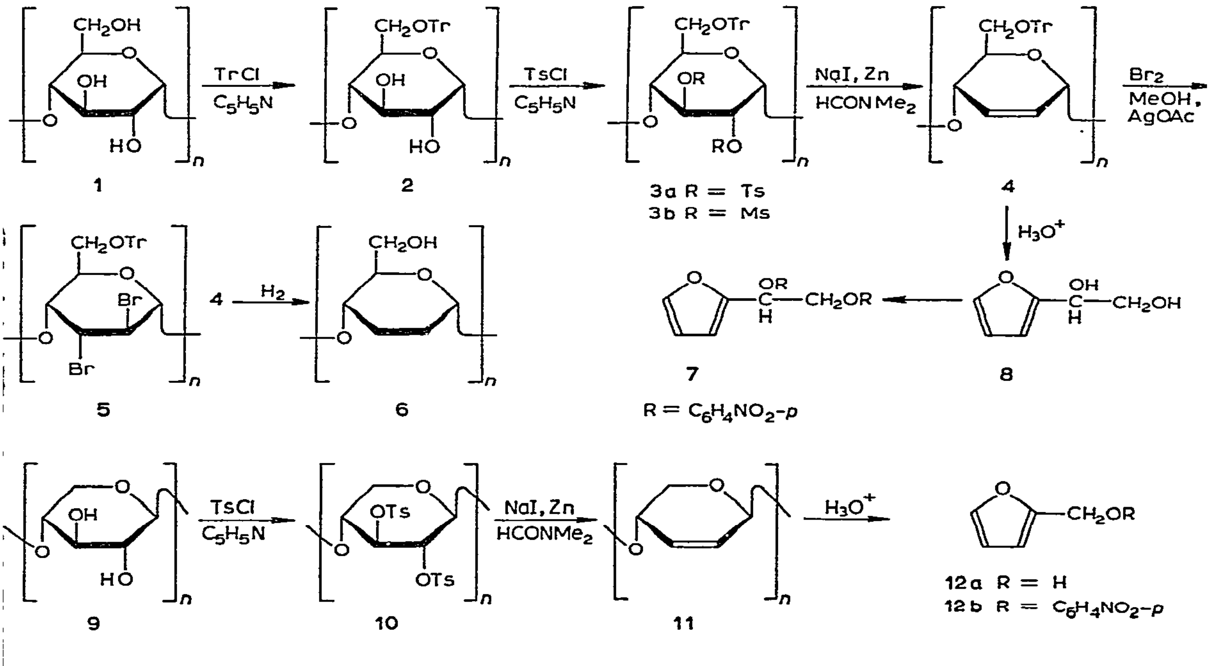
Preparations of **3a** having d.s. 0.8 by trityl and 2.0 by *p*-tolylsulfonyl were subjected to the alkene-forming reaction, and the product gave analytical values[9] indicating d.s. values of 0.8 by trityl and 1.0 by C=C; it is probable that this product contained some 5,6-unsaturated residues together with a preponderance of 2,3-unsaturated residues. The preparation of 5,6-unsaturated amylose has been the subject of a separate investigation[11].

Characterization of **4** having d.s. 1.0 by trityl and 0.75 by the C-2 to C-3 double bond was based on (*a*) the physical and analytical data obtained for the polymer, (*b*) acid-catalyzed degradation of the polymer to give 2-(D-*glycero*-1,2-dihydroxyethyl)furan (**8**), and (*c*) addition reactions to the double bond in the polymer to give dibromo (**5**) and dihydro (**6**) adducts.

Treatment of the unsaturated polymer **4** with 1:3 water–acetic acid for 1 h at 70–80° led to scission of the trityl groups and complete depolymerization, to yield the unstable 2-(D-*glycero*-1,2-dihydroxyethyl)furan[4] (**8**), characterized as its crystalline bis(*p*-nitrobenzoate) (**7**). This reaction course parallels that observed[4] with a monosaccharide 2,3-alkene (methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside) whose preparation and reactions served as a model for the present study. The yield of **8** from **4**, as determined by u.v. spectroscopy of purified[12] **8** from the reaction, was 30%. From the monosaccharide model-compound, the yield of **8** was 90% after a heating period of only 10 min. The lower yield of **8** from **4**, and the need for a longer time of hydrolysis, may result from the fact that formation of the furan is impeded by the presence of a 4-substituent that is cleaved less readily[4,6] than the 4-substituent in the monosaccharide derivative.

Although methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside gives complex mixtures on direct reaction with bromine, it has been shown[13] that the (diaxial) D-*altro* 2,3-dibromide is formed in high yield when bromine is added in the presence of methanol and silver acetate. Under similar conditions, the unsaturated polymer **4** reacted with an excess of bromine to give in 45% yield a pale-yellow powder whose elemental analysis indicated that it contained the proportion of bromine calculated for formula **5**. By analogy with the reaction in the monosaccharide derivative, the D-*altro* stereochemistry may be anticipated for this product, although this point was not established for **5** by any direct experiment.

Reduction of **4** in pyridine with hydrogen and palladium caused saturation of the double bond and partial detritylation. Under more-vigorous conditions, the trityl groups were removed completely, and the absorption of hydrogen was almost 2 molecules per monosaccharide residue, as expected for reduction of the double bond and hydrogenolytic cleavage of the trityl ether group.



The foregoing data for **4**, from analysis, from degradation to **8**, and by addition reactions, provide clear evidence for structure **4**, an unsaturated polysaccharide having a 2,3-double bond.

As an additional polysaccharide model for the alkene-forming reaction, *β*-D-xylan (**9**) was selected; the tritylation step was omitted, because of the absence of a primary hydroxyl group from **9**, obviating possible complications arising from such a protecting group. The xylan[14] **9** reacted with an excess of *p*-toluenesulfonyl chloride to give in high yield the 2,3-bis(*p*-toluenesulfonate) **10**, whose analysis indicated that the d.s. was 2.0 and that no chlorine had been introduced into the molecule.

Treatment of **10** with sodium iodide–zinc dust–*N*,*N*-dimethylformamide as described for **3a** gave a sulfur-free, desulfonyloxylated product formulated as **11**; it was obtained in 82% yield after dialysis of an aqueous suspension of the product. Analysis supported the structure **11** assigned, and the n.m.r. spectrum of **11** in methyl sulfoxide-d_6 showed the signals anticipated (see Experimental section).

The unsaturated polyacetal **11** underwent depolymerization on treatment with 1:3 water–acetic acid, and a syrupy, unstable product that was isolated in 30% yield (as determined by u.v. assay) was identified as furfuryl alcohol[15] (**12a**) and characterized as its known[16], crystalline *p*-nitrobenzoate **12b**. The ready conversion of **11** into **12a** by mild treatment with acid is exactly analogous to the conversion of **4** into **8** and to the corresponding reaction in a monosaccharide analogue[4], and serves as degradative evidence for structure **11**.

The foregoing procedure for introducing alkene-type C-2=C-3 unsaturation into polysaccharides thus appears to be general, being applicable directly with (1→4)-linked pentopyranoglycans; the hexose analogues (such as cellulose) may be expected to require prior protection of O-6 with an ether group.

EXPERIMENTAL

General methods. — Melting points are uncorrected. Optical rotations were measured in a 1-dm tube with a Perkin–Elmer model 141 recording polarimeter. N.m.r. spectra were recorded at 100 and 60 MHz with Varian HA-100 and A-60A spectrometers, with the solvents indicated and tetramethylsilane as the internal reference. Chemical shifts are given on the τ scale. U.v. spectra were recorded with a Beckman DU spectrophotometer. T.l.c. was performed with 0.25-mm layers of Silica Gel G (E. Merck, Darmstadt, Germany); plates were activated at 110°, and sulfuric acid was used for detection (see ref. 12). X-Ray powder diffraction data give interplanar spacings, Å, for CuKα radiation. Relative intensities were estimated visually: m, moderate; s, strong; v, very; w, weak. The strongest lines are numbered in order (1, strongest). The camera diameter was 114.59 mm. Elemental analyses were performed by W. N. Rond.

6-O-Tritylamylose[7,8] (**2**). — Slightly derivatized amylose [Superlose HA-11-HV, Stein–Hall and Co., Inc., New York; a very low d.s. *O*-(hydroxyethyl)amylose of better solubility properties than pure amylose] (18 g) was stirred for 2 h in 95%

aqueous pyridine (450 ml) and the water was removed by repeated evaporation of anhydrous pyridine from the suspension until the distillate no longer became turbid when benzoyl chloride was added. A suspension of the resultant, pyridine-swollen amylose (5 g) in dry pyridine was then heated under reflux on a water-bath at 90–95° with efficient stirring. Chlorotriphenylmethane (13 g) was added in small portions during 15 min, and heating was continued for 2 h. Methanol (150 ml) was then added slowly with stirring, and the resultant, viscous solution was cooled to 25°, poured into methanol (500 ml), and the mixture stirred vigorously. The 6-*O*-tritylamylose (**2**) that separated was collected on a Büchner funnel, washed with methanol, redispersed in methanol with the use of a blender, and filtered off again, washed with methanol, and dried in a vacuum oven at 60° to give a white powder; yield 43 g (96%).

Anal. Calc. for $[C_6H_7O_2(OC_{19}H_{15})_{1.0}(OH)_{2.0}]_n$: C, 74.27; H, 5.97; trityl, 60.10. Found: C, 73.69; H, 5.95; trityl[8], 59.65; Cl, 0.0.

2,3-Di-O-p-tolylsulfonyl-6-O-tritylamylose (**3**). — To a stirred suspension of **2** (5 g) in anhydrous pyridine (50 ml) was added *p*-toluenesulfonyl chloride (80 g) portionwise during 1 h at 60–70°. Stirring was maintained for 3 h at 60–70° and overnight at ~25°. The highly viscous, brown reaction-mixture was poured as a thin stream, with stirring, into a mixture of water (900 ml) and acetone (100 ml). The product separated as a gummy mass from which the supernatant liquor was removed by decantation. The crude product was dispersed in methanol with the use of a blender, and was thereby obtained as a fine, white sediment that was filtered off on a sintered-glass funnel, washed thoroughly with water until free of chloride ions, and dried in a vacuum oven at 60°; yield 8.1 g (97%). The 100-MHz n.m.r. spectrum of this product (**3**) in pyridine-d_5 showed aryl-proton signals at τ 2.3–3.6, signals for protons on the sugar chain at τ 5.4–6.8, and signals for the aryl *C*-methyl groups at τ 8.3, in the approximate intensity-ratios of 23:7:6.

Anal. Calc. for $[C_6H_7O_2(OC_{19}H_{15})_{1.0}(OSO_2C_7H_7)_{1.8}(OH)_{0.2}]_n$: C, 65.72; H, 5.05; S, 8.65. Found: C, 65.51; H, 5.3; S, 8.40; Cl, 0.0.

*2,3-Dideoxy-6-O-trityl-α-*D-erythro*-hex-2-enopyranoglycan* (**4**). — To a suspension of **3** (1.0 g) in *N,N*-dimethylformamide (100 ml) were added sodium iodide (15 g) and zinc dust (7 g), and the mixture was stirred for 6–12 h under reflux at 180–200°. The hot mixture was filtered, and most of the solvent was removed from the filtrate by evaporation at ~95° in a rotary evaporator. Water was added to the residue, and the mixture was dialyzed against running water for 3 days. The resultant suspension was filtered and the solid dried, to give **4** as a pale-brownish powder, yield 0.30 g (58%). The 100-MHz n.m.r. spectrum of **4** in pyridine-d_5 showed two multiplets centered at τ 2.4 and 2.8 (aryl protons) and a series of multiplets between τ 5.0 and 6.8 (protons on the sugar chain) in the approximate ratio of 15:7; aryl *C*-methyl signals were absent.

Anal. Calc. for $[C_4H_5O_2(OC_{19}H_{15})_{1.0}(CH{=}CH)_{0.75}(CHOH{-}CHOH)_{0.25}]_n$: C, 79.23; H, 5.98; trityl, 68.60. Found: C, 78.90; H, 6.03; trityl[8], 68.34; S, 0.0.

2,3-Di-O-(methylsulfonyl)-6-O-tritylamylose (**3b**). — Compound **2** (5.0 g) was dissolved in anhydrous pyridine (100 ml) at 60°. The solution was then maintained at

0° while methanesulfonyl chloride (15 ml) was added portionwise with stirring. After 3 days at room temperature, water (5 ml) was added to the brown solution, followed by acetone (100 ml). The resultant mixture was added, with stirring, to 1:1 acetone–water (400 ml), and the solid filtered off, washed well with water and then 3:1 acetone–water, and dried at 50° *in vacuo* to give **3b** as a pale-brown powder, yield 6.0 g (85%).

Anal. Calc. for $[C_6H_7O_2(OC_{19}H_{15})_{1.0}(OSO_2CH_3)_{2.0}]_n$: C, 57.84; H, 5.03; S, 11.44; Tr, 46.25. Found: C, 57.50; H, 4.71; S, 11.38; Tr, 45.86.

*Degradation of 2,3-dideoxy-6-*O*-trityl-α-*D-erythro-*hex-2-enopyranoglycan* (**4**) *to give 2-(*D-glycero-*1,2-dihydroxyethyl)furan* (**8**). — A suspension of the unsaturated polymer **4** (1.0 g) in 1:3 water–acetic acid (20 ml) was heated for 1 h at 70–80°, whereupon complete dissolution occurred. The cooled solution was kept overnight at ~25° and the crystalline triphenylmethanol that separated was filtered off. The filtrate was evaporated, and the resultant syrup was dissolved in ether and chromatographed on a column of silica gel with ether as eluant. The fractions were examined by t.l.c. on silica gel, with ether as eluant. The first fractions contained triphenylmethanol (yellow color with sulfuric acid). Fractions containing a single component (R_F 0.32, ether) were eluted subsequently, and this component was identified as 2-(D-*glycero*-1,2-dihydroxyethyl)furan (**8**), λ_{max}^{EtOH} 220 nm (ε 8,100); $[\alpha]_D^{24}$ +37.0 ±1° (*c* 1.0, chloroform) [lit.[4] λ_{max}^{EtOH} 218 nm (ε 8,000); $[\alpha]_D^{22}$ +36.7 ±0.4° (chloroform)]. This product (30 mg) was converted[4] into its bis(*p*-nitrobenzoate) **7**; yield 85 mg (85%), m.p. 95–96° (lit.[4] m.p. 95–97°), identical with an authentic sample by mixed m.p. and by i.r. spectrum.

The yield of the furan derivative **8** from the unsaturated polymer **4** was determined to be 30%, as determined by u.v.-spectrometric determination at 220 nm of the product having R_F 0.32 (ether). [A similar determination made for the yield of the furan derivative **8** formed by treatment of methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside with 1:3 water–acetic acid for 10 min at 70° gave a value of 90% (lit.[4] based on isolation of **8**, 87%).]

*2,3-Dibromo-2,3-dideoxy-6-*O*-trityl-α-*D*-hexopyranoglycan* (**5**). — To a suspension of the unsaturated polymer **4** (0.5 g) in pyridine (25 ml) were added silver acetate[13] (0.5 g) and barium carbonate (1.0 g); bromine (1 ml) in methanol (100 ml) was then added dropwise, with stirring, during 30 min at 0°. The mixture was stirred overnight at ~25°, and filtered, the solid was washed with methanol, and air was bubbled through the combined filtrates to remove the excess of bromine. Evaporation of the filtrate gave a thick syrup, addition of methanol to which gave a finely divided precipitate, which was filtered off, successively washed with methanol and water, and dried, to give **5** as a slightly yellow powder; yield 0.32 g (45%). The 60-MHz n.m.r. spectrum of this product in pyridine-d_5 showed multiplets at τ 2.4 and 2.8 (trityl) and at τ 5.0–6.8 (protons on the sugar chain) in the approximate intensity-ratio of 15:7.

Anal. Calc. for $[C_6H_7Br_2O_2(OC_{19}H_{15})_{1.0}]_n$: C, 56.62; H, 4.18; Br, 30.14. Found: C, 56.34; H, 4.54; Br, 30.40.

*2,3-Dideoxy-α-*D-erythro-*hexopyranoglycan* (**6**). — Hydrogen at 1 atm pressure was passed for 24 h at ~25° through a suspension of the unsaturated amylose derivative **4** (0.5 g) in pyridine (50 ml) containing 10% palladium-on-charcoal (0.1 g). The catalyst was filtered off and the filtrate was evaporated. The residue was triturated with methanol, and the resultant solid was filtered off and washed with methanol to give **6** as a pale-brown powder. The methanolic filtrate contained triphenylmethanol and gave a yellow color with sulfuric acid.

Anal. Calc. for $[C_4H_5O_2(OC_{19}H_{15})_{0.5}(OH)_{0.5}(CH_2\text{–}CH_2)_{0.75}(CHOH\text{–}CHOH)_{0.25}]_n$: C, 71.53; H, 6.92. Found: C, 71.81; H, 6.56.

The n.m.r. spectrum of **6** in pyridine-d_5 showed a broad multiplet at τ 4.5–6.8 (protons on the sugar chain) and a multiplet at τ 2.4–2.8 (trityl groups remaining) in the approximate intensity-ratio of 6:5; this result indicated that the product contained residual trityl groups to a d.s. of ~0.5.

In a second experiment, the amount of catalyst used was increased five-fold, and the absorption of hydrogen was measured by use of a closed apparatus with the reaction flask mounted in a shaker. After 4 h at ~25°, ~2 moles of hydrogen/mole had been absorbed, and the n.m.r. spectrum of the product, isolated as before, showed a similar pattern for the ring-proton signals, but the signal for the trityl group was of very low intensity.

*2,3-Di-*O-p*-tolylsulfonyl-β-*D*-xylan* (**10**). — β-D-Xylan (**9**) was obtained from oat hulls and purified by the procedure of Adams[14]; it had $[\alpha]_D^{24}$ −80 ±1° (*c* 1.2, 0.5M sodium hydroxide). To a solution of the xylan (1.0 g) in anhydrous pyridine (100 ml) was added *p*-toluenesulfonyl chloride (10 g) portionwise during 1 h at ~25°, and then the mixture was kept for 6 h at 100°. The solution was poured into a mixture of water (300 ml) and methanol (200 ml) at 0°, the mixture was stirred for 18 h, and the solid product (**10**) was filtered off, washed with methanol, and dried; yield 2.9 g (93%).

Anal. Calc. for $[C_5H_6O_2(OSO_2C_7H_7)_2]_n$: C, 51.80; H, 4.57; S, 14.33. Found: C, 51.28; H, 4.41; S, 14.24; Cl, 0.0.

*2,3-Dideoxy-β-*D-glycero*-pent-2-enopyranan* (**11**). — To a suspension of **10** (1.0 g) in *N,N*-dimethylformamide (100 ml) were added sodium iodide (15 g) and zinc dust (7 g), and the mixture was stirred for 6–12 h under reflux at 180–200° (bath temp.). The hot mixture was filtered, and the filtrate was evaporated *in vacuo* at 100°. Water was added to the residue, and the mixture was dialyzed for 3 days against running water. The solid product was filtered off and dried, to give **11** as a pale-brown powder; yield 0.2 g (82%).

Anal. Calc. for $(C_5H_6O_2)_n$: C, 61.22; H, 6.12. Found: C, 60.65; H, 5.93; S, 0.0.

The 60-MHz n.m.r. spectrum of **11** in methyl sulfoxide showed four distinct multiplets in the ratios of 2:1:2; the first, near τ 3.0 (broad), was assigned to H-2 and H-3. Two 1-proton multiplets, at τ 4.1 and 4.9, were assigned to H-1 and H-4, respectively. A 2-proton multiplet at τ 6.2 was assigned to H-5.

*Degradation of 2,3-dideoxy-β-*D-glycero*-pent-2-enopyranan* (**11**) *to give 2-(hydroxymethyl)furan* (**12a**). — A suspension of the unsaturated polymer **11** (1.0 g) in 1:3 water–acetic acid (20 ml) was heated for 1 h at 70–80°. The resultant mixture was cooled, filtered from a little solid residue, and the filtrate evaporated at 35–40°

to a syrup that was dissolved in ether and chromatographed on a column of silica gel eluted with ether. The fractions that contained a single component having R_F 0.5 [t.l.c., 1:1 ether–petroleum ether (b.p. 30–60°)] were pooled and evaporated, to give 2-(hydroxymethyl)furan[15] (**12a**); optically inactive; $\lambda_{\max}^{\mathrm{EtOH}}$ 225 nm (ε 4,500); $\nu_{\max}^{\mathrm{KBr}}$ 3300 (OH), 2910, 2825 (CH), 1610, 1010, and 880 cm^{-1} (furan); n.m.r. data (60 MHz, chloroform-*d*): τ 2.65 (multiplet, H-5), 3.75 (multiplet, H-3,4), 5.52 (singlet, CH_2), and 6.05 (exchangeable singlet, OH).

The yield of **12a** was 30% as determined by u.v.-spectral assay of the product, in comparison with a standard solution of 2-(hydroxymethyl)furan.

The product was *p*-nitrobenzoylated to give 2-(hydroxymethyl)furan *p*-nitrobenzoate (**12b**), crystallized from methanol, m.p. 78°; $\nu_{\max}^{\mathrm{KBr}}$ 1740 (BzO), 1610 (C=C), 1525 (NO_2), and 1350 cm^{-1} (NO_2); X-ray powder diffraction data: 10.51 m, 5.81 s (2,2), 5.25 vs (1,1), 4.65 s (2,2), 4.33 s (2,2), 4.01 w, 3.77 m, 3.61 m, 3.42 vs (1,1), 3.26 s (2,2), 3.08 m, 2.92 vw, and 2.79 w.

Anal. Calc. for $C_{12}H_9NO_5$: C, 58.30; H, 3.65; N, 5.67. Found: C, 58.17; H, 4.02; N, 5.52.

The product was identical with an authentic sample[16] by mixed m.p., i.r. spectrum, and X-ray powder diffraction pattern.

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