Carbohydrate Research, 61 (1978) 519–528

ACID-CATALYZED PYROLYTIC SYNTHESIS AND DECOMPOSITION OF 1,4:3,6-DIANHYDRO-α-D-GLUCOPYRANOSE*

FRED SHAFIZADEH, RICHARD H. FURNEAUX, THOMAS T. STEVENSON, AND TODD G. COCHRAN
Wood Chemistry Laboratory, Department of Chemistry, University of Montana, Missoula, Montana 59812 (U.S.A.)

(Received August 30th, 1977; accepted for publication in revised form, October 28th, 1977)

ABSTRACT

1,4:3,6-Dianhydro-α-D-glucopyranose (**1**) was formed, together with 1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose (levoglucosenone, **2**) and levoglucosan (**4**), on acid-catalyzed pyrolysis of D-glucose, amylopectin, and cellulose. Pyrolysis of **1** in the presence of acid provided significant quantities of **2**, indicating that **1** can act as a pyrolytic precursor of **2**. A pyrolysis product from cellulose previously considered to be 1,6-anhydro-3-deoxy-β-D-*erythro*-hex-3-enopyranose (**12**) was shown to be the dianhydride **1**.

INTRODUCTION

1,4:3,6-Dianhydro-α-D-glucopyranose† (**1**) was first found as a by-product in the gasification of wood[1]. Subsequently, it was reported as a minor product in the pyrolysis of cellulose, D-glucose, and a variety of D-glucose-containing oligo- and poly-saccharides, and as a major product in the pyrolysis of 3,6-anhydro-D-glucose[2-4]. More recently, it has been detected in the pyrolyzate from cellulose treated with sodium dihydrogenphosphate[5], and in the water-soluble fraction of tobacco smoke[6].

In this laboratory we have been investigating the acid-catalyzed pyrolysis of cellulosic materials for production of levoglucosenone (1,6-anhydro-3,4-dideoxy-β-D-*glycero*-hex-3-enopyranos-2-ulose, **2**)[7,8]. This article reports the isolation of **1** as a by-product and its role as a pyrolytic intermediate.

RESULTS AND DISCUSSION

Isolation and characterization of 1,4:3,6-dianhydro-α-D-glucopyranose (**1**). — Analysis by g.l.c. and t.l.c. of the condensates obtained from pyrolysis of cellulose, D-glucose, and amylopectin containing 0.5–10% of phosphoric acid revealed the presence of levoglucosenone (**2**) and a smaller amount of a less-mobile component. A

---

*Dedicated to Professor Dexter French on the occasion of his 60th birthday.

†Alternatively, this compound may be named 1,5:3,6-dianhydro-β-D-glucofuranose.

crystalline sample of this component was obtained by solvent fractionation and column chromatography of the condensate formed on pyrolysis of cellulose containing 1.5% of phosphoric acid. The melting point, specific rotation, n.m.r. (in D_2O), and mass spectrum obtained for this crystalline product were in close agreement with those previously reported for 1,4:3,6-dianhydro-α-D-glucopyranose[1-4,9] (**1**). Furthermore, hydrolysis of the product with acidic ion-exchange resin gave 3,6-anhydro-D-glucose, which crystallized in 73% yield. Also, acetylation yielded a syrupy monoacetate (single acetoxyl resonance in the n.m.r. spectrum) which, after vacuum-distillation, gave an acceptable elemental analyses for 2-*O*-acetyl-1,4:3,6-dianhydro-α-D-glucopyranose (**3**).

Quantitative analysis of the products. — Analysis by g.l.c. of the acid-catalyzed pyrolyzates after trimethylsilylation revealed the presence of an additional component identified as 1,6-anhydro-β-D-glucopyranose (levoglucosan, **4**). The yields obtained for this compound, and those for **1** and **2**, are listed in Table I. These data show that product yields were dependent upon both the substrate and the pyrolysis conditions employed. Amylopectin gave a higher yield of the dianhydride **1** than did D-glucose or cellulose. This observation parallels that made by Gardiner[3] on the uncatalyzed pyrolysis of various D-glucose derivatives. Pyrolysis under vacuum decreased the yield of **1**, but increased the yield of levoglucosan (**4**), as previously observed in the pyrolysis of untreated cellulose[10]. Increasing the scale of pyrolysis from 1 g to 50 g increased the portion of the condensate not accounted for by **1**, **2**, and **4**. The bulk of this portion has been shown to be polymeric material formed from the monomeric products[10,11]. For laboratory preparations, cellulose is the most suitable of these three substrates because it does not froth during pyrolysis.

Interconversion of the pyrolysis products. — Pyrolysis of carbohydrates involves a series of concurrent and consecutive reactions, including transglycosylation and dehydration. The latter reaction may produce both unsaturated and ether derivatives.

TABLE I

PYROLYTIC PRODUCTION OF 1.4:3,6-DIANHYDRO-α-GLUCOPYRANOSE (1), LEVOGLUCOSENONE (2), AND LEVOGLUCOSAN (4) UNDER NITROGEN AT 350°

Substrate	*H_3PO_4 (%)*[a]	*Pressure*	*Sample weight (g)*	*Char (%)*[a]	*Condensate (%)*[a]	*Percentage of condensate*			*Yield from substrate (%)*[a]		
						1	2	4	1	2	4
Cellulose[c]	1.5	1 atm.	1	39	15	8	47	3	1.2	7.1	0.5
Cellulose[c]	1.5	1.5 torr	1	42	14	5	30	31	0.7	4.2	4.5
Cellulose[d]	1	1 atm.	50	38	10	8	20	1	0.8	2.0	0.1
Amylopectin	1	1 atm.	1	38	21	13	22	11	2.7	4.6	2.3
Glucose	1.5	1 atm.	1	[b]	11	11	38	17	1.2	4.3	1.9

[a] Percent weight, based on the weight of substrate in the original sample. [b] The sample frothed out of the boat. [c] Avicel microcrystalline. [d] Whatman CF-11 powder.

It has been shown that intramolecular transglycosylation of polysaccharides is responsible for their depolymerization to monomeric compounds, which can themselves undergo further transglycosylation, dehydration, disproportionation, and polymerization reactions[10-12].

1,4:3,6-Dianhydro-α-D-glucopyranose (**1**) is formed by a combination of intramolecular transglycosylation and etherification reactions, possibly via 1,4-anhydro-α-D-glucopyranose (**5**) which, together with 1,2-anhydro-α-D-glucopyranose (**6**) and levoglucosan (**4**), has been proposed as a possible, initial depolymerization-product from D-glucose-containing polymers[3,10]. The fact that **1** has been isolated, whereas **5** and **6** remain undetected, is probably due to its high volatility (see later), and also to the relative pyrolytic stability conferred by its 3,6-ether linkage. The stability of such linkages is substantiated by the previous finding of 3,6-anhydro-D-glucose and polymeric material containing 3,6-anhydro groups in the condensates produced on the pyrolysis of cellulose in the presence of acids[11].

The pyrolysis of 1,4:3,6-dianhydro-α-D-glucopyranose (**1**) was examined in order to clarify its role in the sequence of pyrolytic transformations. In the absence of an acid catalyst, heating at 500° resulted merely in the evaporation of **1**. Thermal analysis (Fig. 1) showed that **1** started to sublime at ~100°, melted sharply at 127° (d.t.a.), and continued to vaporize until ~190°, leaving little or no residue. However, thermal analysis of **1** in the presence of diphenyl phosphate* (Fig. 2) showed initial melting of the catalyst at ~60° and of the substrate (**1**) at ~115°, followed by endothermic and then exothermic processes between 125 and 250°. Finally, charring took

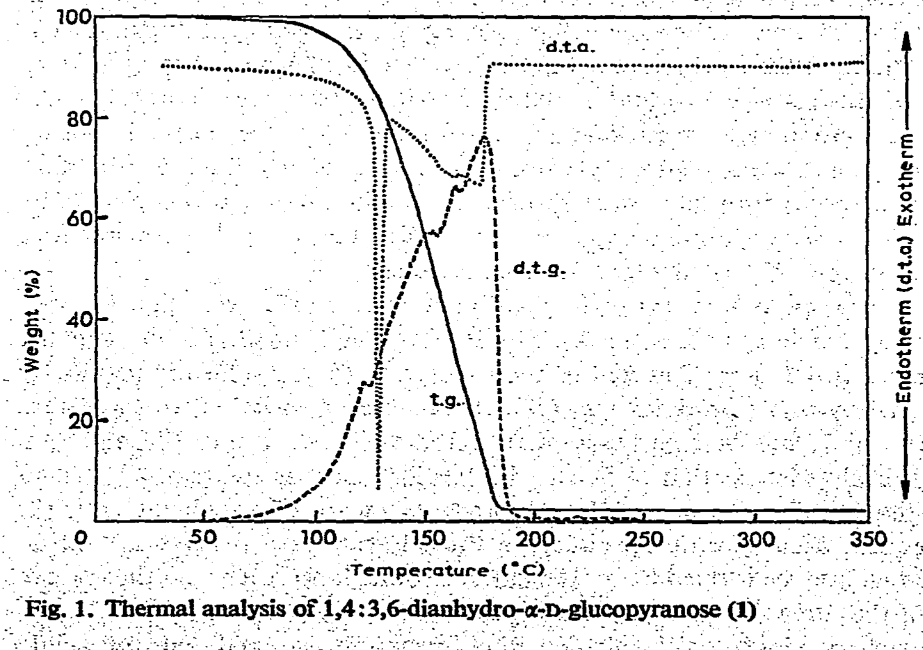


Fig. 1. Thermal analysis of 1,4:3,6-dianhydro-α-D-glucopyranose (**1**)

---

*Employed as a solid Arrhenius acid-catalyst.

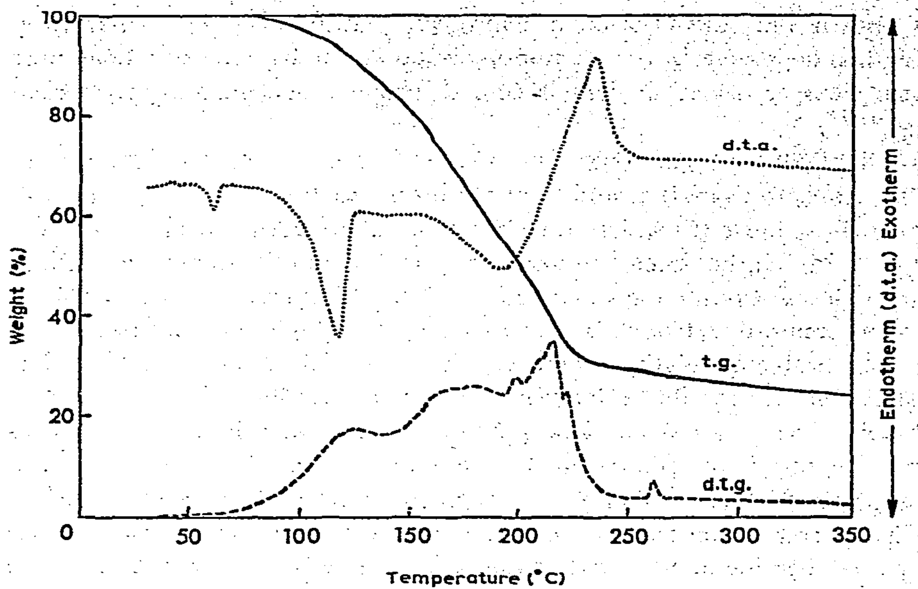


Fig. 2. Thermal analysis of a 9:1 mixture of 1,4:3,6-dianhydro-α-D-glucopyranose (**1**) and diphenyl phosphate.

place and left 25% of residue at 350°. As the endotherm is associated with considerable weight-loss, it is most likely due to volatilization of **1** and its degradation products. Isothermal melt-pyrolysis experiments performed at 200° showed the exotherm to be associated with polymerization involving opening of the 1,4-anhydro linkage of **1**. In the initial stages of the isothermal pyrolysis (1 to 5 min), **1** was shown by t.l.c. to form both 3,6-anhydro-D-glucose and a mixture of oligo- and polysaccharides. These components were gradually converted into water-insoluble char, the conversion being essentially complete after 40 min. Pyrolyzates obtained after 1 and 5 min were hydrolyzed, and the hydrolyzates were shown to contain 3,6-anhydro-D-glucose as the only detectable carbohydrate component, confirming that the polymeric material was composed largely of 3,6-anhydro-D-glucose residues.

When **1** was pyrolyzed through glass-wool coated with phosphoric acid, significant amounts of levoglucosenone (**2**), 2-furaldehyde, and 5-methyl-2-furaldehyde, as well as unchanged **1**, were detected in the pyrolyzate (Fig. 3). Determination of the yields of the pyrolysis products was difficult because of variations in the extent of degradation of **1**, but in eight experiments, the yields of **2** and 2-furaldehyde exceeded 10% each, whereas that of 5-methyl-2-furaldehyde was less than 2%. These results show that the dianhydro sugar **1** can act as a precursor of levoglucosenone (**2**) and its subsequent decomposition-products in the acid-catalyzed pyrolyses. A given pyrolysis product may be formed by more than one route[13], however, and the relative importance of the foregoing pathway in the production of **1** is not known.

As shown previously, 3,6-anhydro ring-formation is catalyzed by acidic reagents[11]. In the case of acid-catalyzed production of the dianhydride **1**, this enhanced

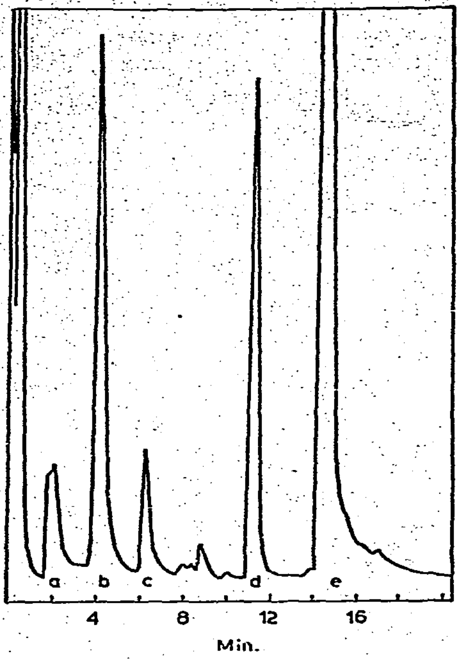
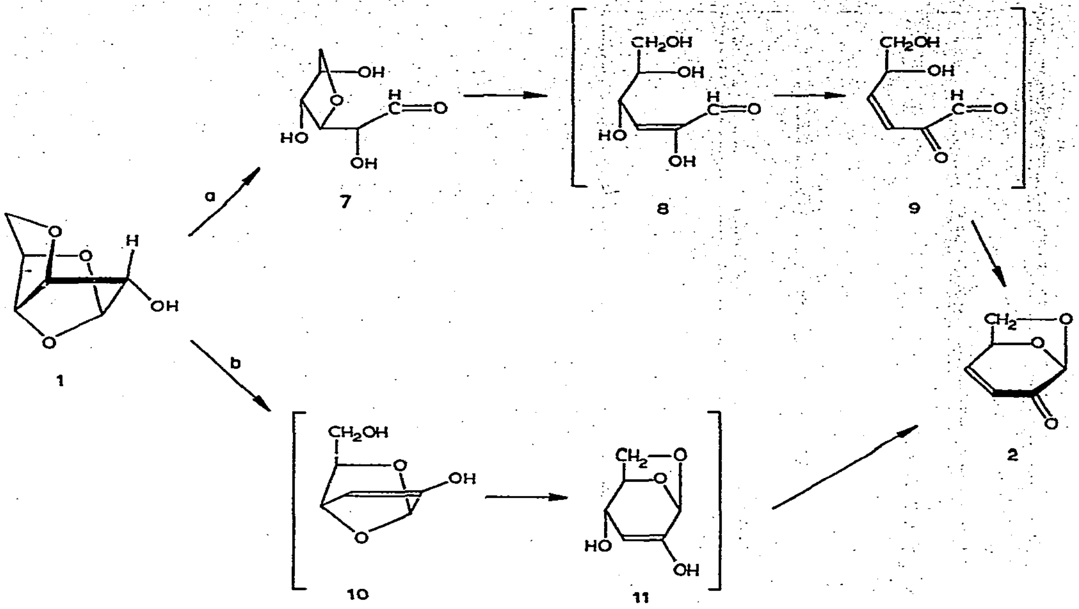


Fig. 3. Chromatogram from direct pyrolysis–g.l.c. of 1,4:3,6-dianhydro-α-D-glucopyranose (1) in the presence of phosphoric acid: a, unknown mixture; b, 2-furaldehyde; c, 5-methyl-2-furaldehyde; d, levoglucosenone (2); e, 1,4:3,6-dianhydro-α-D-glucopyranose (1).

formation must be offset by enhanced decomposition in the presence of acid, as the yields of **1** (Table I) are similar to those reported from uncatalyzed pyrolyses[3].

Production and subsequent degradation of 1,4:3,6-dianhydro-α-D-glucopyranose (**1**) adds a new dimension to the complexity of pyrolytic reactions of carbohydrates. This complexity is not unexpected, as at the high temperatures prevailing during pyrolysis, sufficient energy is available to overcome normal energy-barriers to chemical reaction and rearrangement. Thus, while conversion of **1** to levoglucosenone (**2**) would appear to be rather unusual in terms of normal carbohydrate reactions, the two routes shown in Scheme I are plausible under pyrolytic conditions. Path *a* involves initial hydrolysis to 3,6-anhydro-D-glucose (shown as the aldehydo form **7**), 2,3-elimination of the anhydro ring to the conjugated enol **8**, and dehydration to **9** in a manner well documented for aldohexoses[14], and finally 1,6-anhydro ring-formation from the pyranose tautomer of **9**. Path *b* involves direct 2,3-elimination of the 3,6-anhydro ring to give the enolic intermediate **10**, followed by a (4 → 6) intramolecular transglycosylation and an elimination involving the hydroxyl group at C-4. The formation of 2-furaldehyde and 5-methyl-2-furaldehyde in the pyrolysis of **1** could proceed, at least in part, via **2**, as it has been shown[7] that these two aldehydes are produced on acid-catalyzed pyrolysis of **2**.

Recently, a product isolated from the pyrolysis of cellulose and shown to be a precursor of levoglucosenone[15–17] (**2**), was identified as 1,6-anhydro-3-deoxy-β-D-



Scheme I

erythro-hex-3-enopyranose* (12) based on its molecular formula and spectral characteristics. In our study, it was found that 1,4:3,6-dianhydro-α-D-glucopyranose (1) has identical molecular formula, i.r. and mass spectra, and similar n.m.r., m.p., and optical rotation to those reported for 12, suggesting that these two materials are identical.

Our interpretation of the n.m.r. spectrum of 1 in Me_2SO-d_6 is in accord with those reported[2] for 1 in D_2O, and for its D-*manno*[2] and 2-deoxy-D-*arabino*[18] analogs. A feature common to all three dianhydrides is the unusual deshielding of H-4; the resonance at δ 5.29 thus corresponds to this proton rather than to a vinylic proton as assigned[15,16] for structure 12. Also, the C-2 hydroxyl signal (δ 5.3) of 1 was largely obscured by H-1 and H-4 resonances, but its presence was confirmed by an appropriate one-proton decrease in the integrated peak-area of a deuterated sample of 1 (prepared by dissolving 1 in D_2O, evaporating the solution, and dissolving the residue in Me_2SO-d_6). The difficulties caused by these unusual circumstances have apparently been compounded by the presence of water in the Me_2SO-d_6, which gives a broad absorption at δ 3.4. This resonance, which considerably overlaps the H-2 singlet (δ 3.55) of 1, had been attributed to the carbohydrate hydroxyl protons of 12.

Finally, mixed m.p., t.l.c., and g.l.c. evidence obtained for 1 and a sample of the putative 12 confirmed that these two products were identical.

---

*Named 1,6-anhydro-3-deoxy-β-D-glucopyranosen in refs. 15–17.

EXPERIMENTAL

Acid–substrate mixtures. — The substrate was added to a solution of the required amount of phosphoric acid in methanol, the solvent was evaporated under diminished pressure at 40°, and the residue was dried *in vacuo* at 50°. A 1:9 mixture of diphenyl phosphate and 1,4:3,6-dianhydro-α-D-glucopyranose (**1**) was obtained by grinding these compounds together in a mortar.

Pyrolysis conditions. — Samples (1 g) were pyrolyzed at 350° in a 1 × 7-cm aluminum-foil boat inside a 1.5-cm (i.d.) pyrex-glass tube, whereas 50-g samples were pyrolyzed in a 4 × 13-cm aluminum boat inside a 4.5-cm (i.d.) pyrex-glass tube. The pyrolysis tube was swept either by a 200 ml.min^{-1} nitrogen flow at atmospheric pressure or by a gentle stream of nitrogen maintained at a pressure of 1.5 torr by a high-vacuum pump. After completion of pyrolysis (5 min for 1 g, 30 min for 50 g), the distillate that collected in a water-cooled condenser was dissolved in methanol, and the mixture was filtered. The filtrate was evaporated to a syrup, and the residue was taken up in abs. ethanol, and the solution finally evaporated *in vacuo* at 40° to a syrup.

G.l.c. of the pyrolysis condensates. — Underivatized condensates were analyzed on a stainless-steel column [1.1 m × 4.3 mm (i.d.)] packed with 5% Carbowax 20M (TPA) on 80–100 mesh Gas–Chrom Q, using phenyl tetra-*O*-methyl-β-D-glucopyranoside as an internal standard, with the injector at 230°, and the column programmed from 100 to 235° at 8°/min. Trimethylsilylated condensates (prepared by using TriSil reagent, Pierce Chemical Co.) were analyzed on a stainless-steel column [1.8 m × 2.2 mm (i.d.)] packed with 3% of SE-52 on 100–120 mesh Gas–Chrom Q, using *myo*-inositol as an internal standard, with the injector at 255°, and the column programmed from 100 to 275° at 8°/min. Both analytical methods employed hydrogen flame-ionization detection, digital integration, and nitrogen as the carrier gas. Compounds were identified by comparison of their retention times and g.l.c.–mass spectral characteristics with those of authentic samples.

T.l.c. of the pyrolysis condensates. — Analyses were performed on silica gel eluted with solvent *A* (3:2 ethyl acetate–dichloroethane) or solvent *B* (5:4:1 acetone–ethyl acetate–water); carbohydrates were detected by using an 3:5:95 anisaldehyde–sulfuric acid–ethanol spray-reagent and heating at 120°.

Thermal analysis. — The t.g., d.t.g., and d.t.a. data were obtained as previously reported[7].

Phenyl tetra-O-methyl-β-D-glucopyranoside (g.l.c. internal standard). — Purdie methylation[19] of phenyl β-D-glucopyranoside (Sigma Chem. Co.) yielded a syrup that crystallized from acetic acid–water and was recrystallized from petroleum ether at −10° to yield the tetramethyl ether as white needles, m.p. 76–77° [lit.[20] m.p. 77°].

1,4:3,6-Dianhydro-α-D-glucopyranose (**1**). — A mixture of cellulose (Avicel microcrystalline, 215 g) and phosphoric acid (1.5% by weight) was pyrolyzed in four batches at 360–385° at 1.5 torr. The condensate (35 g) was partitioned between water and dichloromethane, and the aqueous fraction was evaporated to a dark-brown syrup (15 g). This syrup was extracted with ethyl acetate (200 ml) and the extract evaporated to a light-brown syrup (10 g) that was partitioned on a column of silica gel (150 g) eluted with 1:2 ethyl acetate–light petroleum ether. Fractions judged by t.l.c. (solvent *A*) to contain largely the dianhydro sugar **1** (R_F 0.25, red-brown) were combined and evaporated to a syrup (1.8 g) that crystallized from ethyl acetate–hexane (0.66 g). A further crop (0.25 g) was obtained after further chromatographic fractionation of the mother liquors, affording an overall yield of 0.5% from cellulose. The combined crops were treated with activated charcoal in hot ethyl acetate and recrystallized from ethyl acetate–hexane to yield the dianhydro sugar **1** as white crystals, m.p. 127.5–128°, $[\alpha]_D$ +77° (*c* 1.4, ethanol), $[\alpha]_D$ +67° (*c* 1.6, water) [lit.[1–3] m.p. 127–128°, 122–123°, 126°, $[\alpha]_D$ +65.7° (*c* 1.2, water)] (Found: C, 49.8; H, 5.6. $C_6H_8O_4$ calc: C, 50.0; H, 5.6%); *m/e* 144 (7%, M^+), 115 (1), 114 (4), 99 (15), 98 (15), 97 (4), 96 (8), 95 (6), 86 (11), 85 (11), 73 (13), 71 (15), 70 (25), 69 (100), 60 (15), 57 (42), and 55 (10%); ν_{max}^{KBr} 3365, 3020, 2980, 2960, 2930, 2895, 2870 (shoulder), and 1065 cm^{-1}; n.m.r. (δ, Me_2SO-d_6) 3.4 (H_2O), 3.55 (s, 1H, H-2), 3.88 (d, 2H, H-6,6′, *J* 1.3 Hz), 3.98 (dd, 1H, H-3, $J_{1,3}$ 1.2, $J_{3,4}$ 4.5 Hz), 4.18 (m, 1H, width 6 Hz, H-5), 5.3 (broad, 1H, OH), 5.29 (dd, 1H, H-4, $J_{4,5}$ 3.7 Hz), and 5.37 (d, 1H, H-1). A sample of the compound reported[15–17] as **12** had t.l.c. (solvent *A*) and g.l.c. (Carbowax 20M TPA) characteristics identical to those of **1**, and mixed m.p. with **1**, 128–129° [lit.[15–17] m.p. 130–131°, $[\alpha]_D$ +86° (*c* 0.6, ethanol)].

2-O-Acetyl-1,4:3,6-dianhydro-α-D-glucopyranose (**3**). — Compound **1** (0.16 g) was dissolved in pyridine (2 ml) and acetic anhydride (2 ml) and kept overnight at room temperature, after which time t.l.c. indicated its complete conversion into a more-mobile product. After addition of methanol (5 ml), the solvent was evaporated *in vacuo* at 50°, residual pyridine being removed by azeotropic distillation with toluene, yielding monoacetate **3** as a thin, light-yellow syrup. Vacuum distillation (0.7 torr, oil bath at 120°) yielded a colorless syrup $[\alpha]_D$ +92° (*c* 1, chloroform) (Found: C, 51.4; H, 5.2. $C_8H_{10}O_5$ calc.: C, 51.6; H, 5.4%); *m/e* 186 (9%, M^+), 156 (3), 144 (2), 143 (12), 141 (2), 127 (1), 126 (1), 115 (5), 114 (9), 99 (2), 98 (17), 97 (7), and 69 (100%); n.m.r. (δ, $CDCl_3$) 5.56 (s, 1H, H-1), 5.21 (dd, 1H, $J_{3,4}$ $\sim J_{4,5}$ $\sim$4 Hz, H-4), 4.60 (s, 1H, H-2), 4.27 (m, 2H, H-3,5), 4.06 (broad s, 2H, H-6,6′), and 2.12 (s, 3H, OAc).

Hydrolysis of 1,4:3,6-dianhydro-α-D-glucopyranose (**1**) *to 3,6-anhydro-D-glucose.* — Compound **1** (0.153 g) in water (7 ml) was stirred with Dowex 50W-X8 cation-exchange resin (H^+, ~1 cm^3) at 97°. After 4 h, t.l.c. indicated complete conversion into a less-mobile product. The mixture was filtered, taken to dryness, and the residue was crystallized from 1:1 ethanol–ethyl acetate with hexane added to incipient turbidity, yielding 3,6-anhydro-D-glucose as white needles (0.125 g, 73%). Recrystallized from the same solvent, it had m.p. 120–121°, $[\alpha]_D$ +50° (*c* 0.9, water) [lit.[21], m.p. 122°, $[\alpha]_D$ +55° (*c* 2.9, water)]. This product did not depress the m.p. of an authentic sample[22].

Pyrolysis of 1,4:3,6-dianhydro-α-D-glucopyranose (**1**). — *A. Melt pyrolysis.* Samples (2 mg) of a 1:9 diphenyl phosphate–**1** mixture were heated at 200° for 1-, 3-, 5-, 10-, 20-, and 40-min periods. The residues were then dissolved in water (0.15 ml) and analyzed by t.l.c. with solvents *A* and *B*. Qualitatively identical results were obtained, whether the samples were heated in open aluminum pans or in capillary tubes (either sealed or open). Samples from 1- and 5-min pyrolyses were hydrolyzed in 0.6M sulfuric acid for 3 h at 97°, neutralized with barium carbonate, centrifuged, and the resulting solution was analyzed by t.l.c. Components were assigned as **1** or 3,6-anhydro-D-glucose by comparison of their R_F values with those of authentic samples.

B. Direct pyrolysis–g.l.c. Crystalline samples of **1** (1–2 mg) were pyrolyzed in 1.5 × 10 mm capillary tubes in a pyrolysis apparatus interfaced directly with the inlet port of a gas chromatograph. In the experiments involving acid catalysis, a small glass-wool plug was placed in the open end of the capillary and coated with 1–2 μl of 85% phosphoric acid. The capillary was heated by a surrounding wire coil to 500° in approximately 10 sec, the temperature being monitored with a thermocouple. The pyrolysis effluent was swept by the nitrogen carrier gas directly into the stainless-steel g.l.c. column [2 m × 2.2 mm (i.d.)] packed with 3% Silar 5CP on 80–100 mesh Gas–Chrom Q, with injector at 255°, and column programmed from 100 to 250° at 10°/min. The eluted components were identified by comparison of their retention times and g.l.c.–mass spectral characteristics with those of authentic samples.

ACKNOWLEDGMENTS

The authors are grateful to the National Science Foundation for supporting this work under Grant No. AER75-15930. They also thank Dr. Akio Ohnishi for a sample of his pyrolysis product, and Dr. G. N. Richards for helpful discussions.

REFERENCES

1 D. Tischenko and N. Nosova, *Zh. Obshch. Khim.*, 18 (1948) 1193–1197.
2 G. R. Bedford and D. Gardiner, *Chem. Commun.*, (1965) 287–288.
3 D. Gardiner, *J. Chem. Soc., C*, (1966) 1473–1476.
4 K. Heyns, R. Stute, and H. Paulsen, *Carbohydr. Res.*, 2 (1966) 132–149.
5 P. Köll, T. Schultek, and R.-W. Rennecke, *Chem. Ber.*, 109 (1976) 337–344.
6 J. N. Schumacher, C. R. Green, F. W. Best, and M. P. Newell, *J. Agric. Food Chem.*, 25 (1977) 310–320.
7 F. Shafizadeh and P. P. S. Chin, *Carbohydr. Res.*, 46 (1976) 149–154.
8 F. Shafizadeh and P. P. S. Chin, *Carbohydr. Res.*, 58 (1977) 79–87.
9 K. Heyns and H. Scharmann, *Carbohydr. Res.*, 1 (1966) 371–392.
10 F. Shafizadeh and Y. L. Fu, *Carbohydr. Res.*, 29 (1973) 113–122.
11 F. Shafizadeh, Y. Z. Lai, and C. R. McIntyre, *J. Appl. Polym. Sci.*, in press.
12 F. Shafizadeh, *Appl. Polym. Symp.*, 28 (1975) 153–174.
13 F. Shafizadeh and Y. Z. Lai, *J. Org. Chem.*, 37 (1972) 278–284.
14 E. F. L. J. Anet, *Adv. Carbohydr. Chem.*, 19 (1964) 181–218; W. M. Corbett and J. Kenner, *J. Chem. Soc.*, (1957) 927–928.
15 A. Ohnishi, E. Takagi, and K. Kato, *Chem. Lett.*, (1974) 1361–1362.
16 A. Ohnishi, K. Kato, and E. Takagi, *Polymer J.*, 7 (1975) 431–437.
17 A. Ohnishi, E. Takagi, and K. Kato, *Bull. Chem. Soc. Jpn.*, 48 (1975) 1959–1960.

18 J. S. Brimacombe, I. Da'Aboul, L. C. N. Tucker, N. Calvert, and R. J. Ferrier, *Carbohydr. Res.*, 27 (1973) 254–256.

19 E. L. Hirst and E. Percival, *Methods Carbohydr. Chem.*, 2 (1963) 145–150.

20 B. E. C. Banks, Y. Meinwald, A. J. Rhind-Tutt, I. Sheft, and C. A. Vernon, *J. Chem. Soc.*, (1961) 3240–3246.

21 B. A. Lewis, F. Smith, and A. M. Stephen, *Methods Carbohydr. Chem.*, 2 (1963) 172–188.

22 Y. Z. Lai and F. Shafizadeh, *Carbohydr. Res.*, 38 (1974) 177–187.