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AN IMPROVED PREPARATION OF 3-DEOXY-D-*erythro*-HEXOS-2-ULOSE *VIA* THE BIS(BENZOYLHYDRAZONE) AND SOME RELATED CONSTITUTIONAL STUDIES*

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ABSTRACT

Sugar osazones and glycosuloses rapidly and quantitatively react with hydroxylamine to produce oximes that give trimethylsilyl derivatives suitable for g.l.c. and mass spectral analysis. The reaction of D-glucose with benzoylhydrazine to give the bishydrazone of 3-deoxy-D-*erythro*-hexos-2-ulose (**1**) [H. El Khadem *et al.*, *Carbohydr. Res.*, 22 (1973) 381–89] was re-investigated, together with the conversion of this compound to the hexosulose. Although by-products are produced in the reaction, including the bis(benzoylhydrazone) (osazone) of D-glucose, the major product is the monohydrate of the bis(benzoylhydrazone) of **1** (colorless). The anhydrous (yellow) form can be prepared from the monohydrate by crystallization from absolute ethanol and has quite different physical properties. Improvements of the original preparation are described that allow the preparation of the bishydrazone and its subsequent conversion to **1** *via* transhydrazonation in 44% overall yield, and with no detectable contamination by D-glucose or D-glucosone. Evidence is presented that the previously reported cyclic form of the bis(benzoylhydrazone) of D-glucose is the bis(benzoylhydrazone) (monohydrate) of **1**.

INTRODUCTION

In both alkaline degradation reactions and in the acid-catalyzed dehydration of D-glucose, 3-deoxy-D-*erythro*-hexos-2-ulose (**1**) has been shown to be an important intermediate[1,2], in the former instance for metasaccharinic[1] acid formation, and in the latter for 2-furaldehyde formation. Although it has limited stability, **1** has been isolated and characterized[3,4]. Among the preparations described for **1** are the interaction of D-glucose with 1-butylamine[5] and the decomposition of the compound produced *in situ* [presumably 1-(1-butyl)-1-deoxy-D-fructose]; the decomposition of "difructose glycine"[5], also an Amadori compound; and the direct conversion of D-glucose to the bis(benzoylhydrazone), which is reported[6,7] to be isolated in pure,

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crystalline form and which can be converted to **1** by transhydrazonation with benzaldehyde. Our interest in obtaining gram amounts of **1** prompted us to investigate the last-mentioned procedure, originally described by El Khadem *et al.*[6,7], because these procedures do not involve chromatographic separation. The reaction as described by these workers has been difficult to study from a quantitative standpoint because analytical methods for **1** and for hydrazones derived from **1** were not available.

The purpose of the present paper is to report the improvement of yield and purity in the preparation of **1** as originally described by El Khadem *et al.*[6,7], and to report the application of some analytical procedures that allow the examination of bishydrazones and glycosuloses, such as **1**, by g.l.c. and mass spectral analysis. In addition, some conclusions reported in earlier papers[8] with respect to proposed products in this reaction were found to be in error, and are corrected using these methods.

RESULTS AND DISCUSSION

Attempts to produce the bishydrazone of **1** by use of published procedures gave materials that showed variations in physical constants. A complex mixture of components for such preparations would not be surprising as reports have been

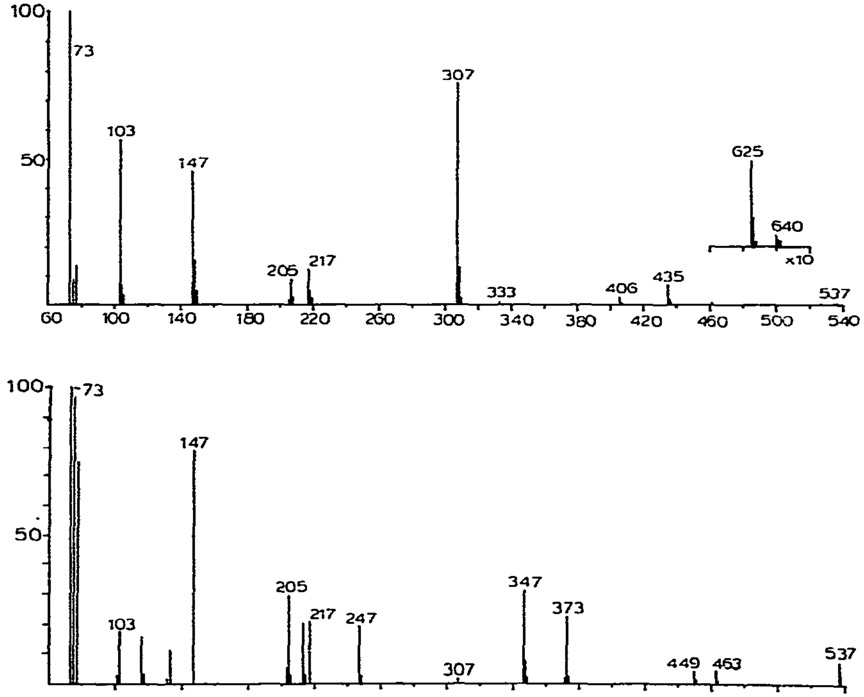


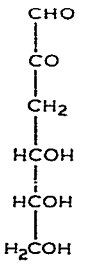
Fig. 1. Mass spectra of per-*O*-trimethylsilyl 1,2-dioxime derivatives of **2**(**4**) (upper) and **1**(**3**) (lower).

published suggesting anhydrous[7] and hydrated[7] forms, as well as cyclic[8] and acyclic[9] bishydrazones of D-glucose being produced.

Initial efforts, therefore, involved attempts to separate and analyze components of this mixture, as well as the identification of transhydrazonation products. Previous work in this laboratory[10,11] showed that carbonyl-containing compounds, such as amino sugars, neutral sugars, and sialic acids[12], react with hydroxylamine or *O*-methylhydroxylamine to give oximes, which, on trimethylsilylation, provide derivatives suitable for analysis by g.l.c., and show sufficient fine structure of mass spectra to permit the definitive structural assignment of these derivatives.

For the quantitative determination of D-*arabino*-hexos-2-ulose[13] and 3-deoxy-D-*erythro*-hexos-2-ulose[7] (**2**) by g.l.c., the per-*O*-trimethylsilyl-*O*-trimethylsilyl-1,2-dioxime derivatives proved to be superior to the corresponding per-*O*-(trimethyl)silylated O-methyl-1,2-dioxime derivatives, since single peaks were obtained with g.l.c. solution of 2% of GC-SE-30 and 1.5% of GC-SE-52 on Chromosorb W.H.P. (100–120 mesh). Oximation of the hexos-2-uloses was typically complete in less than 15 min, and trimethylsilylation with 1:1 (v/v) *N*,*O*-bis(trimethylsilyl)trifluoroacetatamide–*N*-trimethylsilylimidazole was complete upon dissolution. A standard deviation <3% was obtained for 1–4 μg of injected hexos-2-ulose. Amounts, however, as low as 0.3 μg of hexos-2-ulose could be measured by g.l.c.

In the mass spectral analysis of the per-*O*-(trimethyl)silyl-1,2-dioximes (**3** and **4**) of the two hexos-2-uloses (**1** and **2**, respectively) (see Fig. 1), a molecular ion <15 *m/z* units, characteristic of trimethylsilylated compounds, gave rise to ions at *m/z* 625 and 537 for **2** and **1** derivatives, respectively. As with the *O*-methyldioximes[14], the most prominent fragments for the per-*O*-(trimethyl)silyldioxime (**4**) of **2** are due to β and γ fragmentation, with charge retention on the non-nitrogen-containing fragment preferred, giving ions of large relative abundance at *m/z* 307, 217 (307 — 90), and 103. Major fragmentation for the 3-deoxy analog (**3**), however, occurs in position β to the methylene carbon to give *m/z* 347, with charge retention on the nitrogen-containing fragment, although ions at *m/z* 217, 205, and 103 are prominent as well.



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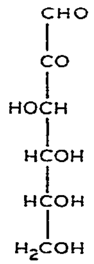

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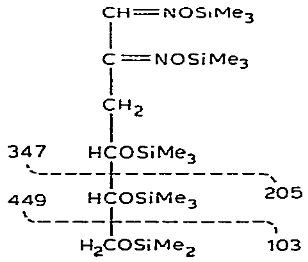

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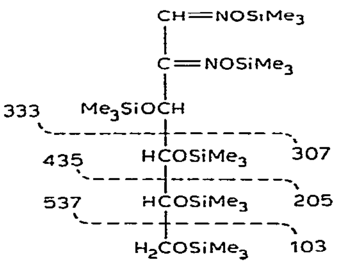

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Modifications of oximation–trimethylsilylation procedures used for the aldos-2-uloses converted D-glucose phenylosazone to the per-*O*-trimethylsilyl-1,2-dioxime derived from **2**, directly. This conversion was found to be of general use, and the

TABLE I

RETENTION TIMES FOR THE PER-*O*-(TRIMETHYL)SILYL 1,2-DIOXIMES OF SELECTED HEXOS-2-ULOSES AND HEXOS-2-ULOSE BIS(ARYLHYDRAZONES)

Starting compound	*Retention time*[a] *(min)*		
	A	*B*	*C*
D-*arabino*-Hexos-2-ulose (**2**)	18.4	11.8	8.8, 9.0
3-Deoxy-D-*erythro*-hexos-2-ulose (**1**)	14.0	11.0	6.5, 7.3
D-*arabino*-Hexos-2-ulose bis(phenyhydrazone)	18.4	11.8	8.8, 9.0
3-Deoxy-D-*erythro*-hexos-2-ulose bis(benzoylhydrazone)	14.0	11.0	6.5, 7.3
3-Deoxy-D-*erythro*-hexos-2-ulose bis(benzoylhydrazone) monohydrate	14.0	11.0	6.5, 7.3
Cyclic D-*arabino*-hexos-2-ulose bis(benzoylhydrazone) preparation[8]	14.0	11.0	6.5, 7.3

[a] Conditions: SE-52 liquid phase (see Experimental section), 150° isothermal; B, SE-30 liquid phase (see Experimental section), programmed from 125–220°, 8°/min with a 2-min initial hold; and C, SP-2250 liquid phase (see Experimental section), programmed from 150–220°, 6°/min with a 2-min initial hold.

bis(benzoylhydrazone) of **1** reacted similarly, as evidenced by mass spectrometry and identical peaks in several g.l.c. columns. Retention times for the derivatives obtained from **1**, **2**-D-glucose phenylosazone, and related compounds, are shown in Table I.

Oximation of the bis(benzoylhydrazones) tested was complete in less than 30 min. However, oximation of D-glucose phenylosazone required 4 h. The dioximes derived from bishydrazones required longer trimethylsilylation times, as well, as *N*-trimethylsilylimidazole was excluded owing to its interference with the silylation of the liberated hydrazines. The chromatograms resulting from the derivatization of D-glucose phenylosazone and the bis(benzoylhydrazone) of **1** (monohydrate), are shown in Fig. 2, the latter peaks corresponding to the per-*O*-trimethylsilyl-1,2-dioximes (**3** and **4**), whereas the peaks with shorter retention time correspond to trimethylsilylated benzoylhydrazine and phenylhydrazine. The liberation of benzoylhydrazine when bis(benzoylhydrazones) were derivatized was confirmed by mass spectrometry. The mass spectra show fragments at *m/z* 280 (M^+), 265 (280 — 15), and 105 (acylium$^+$) characteristic of the *N*,*N*-bis(trimethylsilyl) derivatives of benzoylhydrazine.

By use of the aforementioned separation and quantitative determination techniques, preparations of the bis(benzoylhydrazone) of **1** were examined. The preparations were contaminated by **2** (presumably the bishydrazone) and D-glucose (either the hydrazone or free aldose) to at least a level of 6%. In subsequent experiments, it was found that modifications of original procedures permitted a preparation

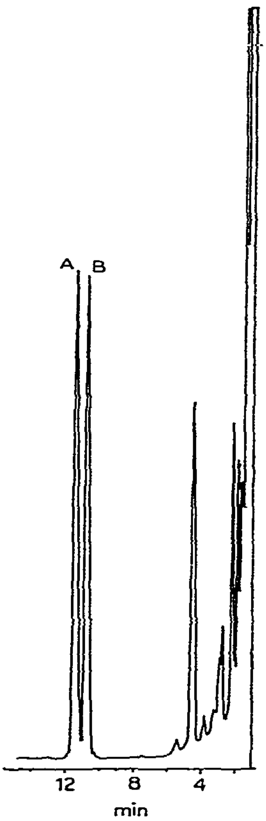

Fig. 2. A typical g.l.c. separation of per-*O*-trimethylsilyl-1,2-dioximes of D-*arabino*-hexos-2-ulose (4) (A) and 3-deoxy-D-*erythro*-hexos-2-ulose (3) (B) starting from the bishydrazones. Faster emerging peaks correspond to trimethylsilyl derivatives of benzoylhydrazine, phenylhydrazine, and related decomposition products.

of the bishydrazone of **1** with no contamination by D-glucose or **2** detectable by g.l.c. These modifications include (see Experimental section) reduction of the solvent volume during bishydrazone formation, reduction of the amount of acetic acid used during transhydrazonation, and the use of a strongly basic, ion-exchange resin charged completely in the carbonate form to neutralize the reaction mixture. With these modifications, the overall yield of **1** (starting from D-glucose) was 44%. Analysis indicated a contamination by **2** and D-glucose of less than 0.06 and 0.2%, respectively. Elemental analysis (Experimental section) clearly indicated that it is a monohydrate. Other data include a 60-MHz ^{1}H-n.m.r. spectrum for a dimethyl sulphoxide-d_6 solution showing peaks (relative to tetramethylsilane) at δ 11.8, 11.9 (NH), 8.05 (H-1), 9.0–7.23 (aryl, and 3.0–2.6 (m, H-3), as well as u.v. (λ_{max} 321 and 206) and i.r. (3420, 3300, and 1645 cm^{-1}) spectra. The bishydrazone monohydrate of **1**, consumed 1.8 mol of periodate per mol. Both 4- and 5-carbon products of periodate oxidation were identified by mass spectrometry following conversion to the per-*O*-(trimethyl)-

silyltrioximes. The 5-carbon trioxime produced a molecular ion at *m/z* 463, and a prominent fragment at *m/z* 218, which corresponds to a β fragmentation between C-3 and C-4, with charge retention on the C-4–5 fragment. The 4-carbon trioxime also produced a molecular ion at *m/z* 361. Details of these spectra as well as methods for the isolation of the oxidation products are described in the Experimental section.

When the bis(benzoylhydrazone) monohydrate of **1** was recrystallized from anhydrous ethanol to give a constant melting point, the anhydrous material was obtained; it showed an ^{1}H-n.m.r. spectrum, except for an absent water signal, identical to that of the monohydrate. When this compound was converted to the per-*O*-(trimethyl)silyl dioxime derivative, it produced identical g.l.c. peaks and m.s. fragmentation corresponding to the derivatives prepared from the monohydrate, as well as from **1**.

The melting points and optical rotations originally reported[6] for this compound are intermediate between those found in this work for the monohydrate and the anhydrous form, respectively. This suggests that the preparation may, in fact, have been a mixture of the two, with additional contaminants. The striking difference in optical rotation between the monohydrate (+7.5°) and the anhydrous form (+40°) suggests that these two forms may have quite different structures or conformations in pyridine solution. With the exception of the optical rotation, the other physical properties of the bishydrazone monohydrate (melting point, u.v. and i.r. spectra), and chemical properties (elemental analysis, periodate consumption) are in reasonable agreement with those reported by El Khadem *et al.*[8] for the cyclic form of D-glucose bis(benzoylhydrazone). Both the monohydrate and the reported cyclic forms consume the same amount of periodate per mole, and differences between the elemental formulas are so slight that they would not be reflected in an elemental analysis. Unfortunately, original samples were not available, but when the preparation was repeated as described in the original report[8], and the isolated product derivatized for g.l.c., the product was the bis(benzoylhydrazone) of **1**, as evidenced by m.s. fragmentation and coincident g.l.c. peaks. Thus, for the case of D-glucose, the reaction product appears to be the bis(benzoylhydrazone) monohydrate of **1** and not the cyclic form of D-glucose bis(benzoylhydrazone).

EXPERIMENTAL

General methods. — Melting points were determined with a Thomas–Hoover Uni-Melt apparatus and are uncorrected. Optical rotations were measured in 1-dm tubes with a Franz, Schmidt, and Haensch polarimeter. I.r. spectra were recorded with a Perkin–Elmer 237B or Backman Acculab-1, double-beam spectrophotometer. ^{1}H-N.m.r. spectra were recorded at 60 MHz with a Varian T-60 or Varian 360-L spectrometer, with tetramethylsilane or sodium 3-(trimethylsilyl)propanesulfonate as internal standards. G.l.c. was performed with a Perkin–Elmer Sigma 3 chromatograph equipped with the following nickel columns (0.3 × 150 cm): (*A*) 1.5% of GC-SE-52 silicone rubber (Varian Aerograph) on 100/120 mesh Chromosorb W, H.P.; (*B*) 2% of GC-SE-30 silicone rubber (Alltech Associates, Inc., Deerfield, IL 60015) on 100/120 mesh Chromosorb W, H.P.; and (*C*) 3% of SP-2250 on 80/100 mesh Supelcoport (Supelco, Inc., Bellefonte, PA 16823); nitrogen flow rates, and detector and injector temperatures were 24 mL/min and 240°, respectively. For m.s. studies, the g.l.c. columns were placed in an H and F chromatograph interfaced with a CEC model 21-110C mass spectrometer having a 70 eV ionization potential. Microanalyses were performed by Galbraith Laboratories, Knoxville, TN 37921.

3-Deoxy-D-erythro-*hexos-2-ulose bis(benzoylhydrazone).* — The monohydrate was prepared by modifications of the procedures reported by El Khadem *et al.*[6,7]. A solution of D-glucose (20 g) and *p*-toluidine (11 g) in a mixture of 95% ethanol (450 mL) and acetic acid (22 mL) was boiled under reflux for 30 min. To this solution was added benzoylhydrazine (33 g), and the reflux was continued for 7 h. The solution was allowed to cool to 25° with stirring. The product that separated after 12 h was collected by filtration, washed with methanol (3 × 100 mL), ether (3 × 100 mL), and methanol (3 × 100 mL), and air dried, to give 21.4 g of material. Recrystallization from 95% ethanol (1.2 L) gave a product having m.p. 172–173°, $[\alpha]_D^{22}$ +7.5° (*c* 0.53, pyridine); ν_{max}^{KBr} 3420 (OH), 3300 (OH), and 1645 cm^{-1} (CONH); λ_{max}^{EtOH} 321 (4.53), 239 (4.19), and 206 (4.29). ^{1}H-n.m.r. (dimethyl sulfoxide-d_6); δ 11.9 and 11.8 (2s, NH, disappears on addition of triethylamine and D_2O), 8.05 (s, H-1), 7.90–7.23 (m, aryl), 3.90–3.0 (m, H-4, -5, -6, and -6′), 3.20 (s, H_2O), and 3.00–2.60 (m, H_2-3).

Anal. Calc. for $C_{20}H_{22}N_4O_5 \cdot H_2O$: C, 57.7; H, 5.8; N, 13.5. Found: C, 57.7; H, 5.9; N, 13.5.

The anhydrous form was prepared by recrystallization from 100% ethanol, yellow, m.p. 228–229°, $[\alpha]_D^{22}$ +40° (*c* 0.53, pyridine).

Anal. Calc. for $C_{20}H_{22}N_4O_5$: C, 60.3; H, 5.6; N, 14.1. Found: C, 60.3; H, 5.7; N, 14.1.

Per-O-(trimethyl)silyl oxime derivatives of hexos-2-uloses and hexos-2-ulose bis(arylhydrazones), and periodate oxidation of products derived therefrom. — Hexos-2-uloses (0–2 mg), hexos-2-ulose bis(arylhydrazones) (0–5 mg), or periodate oxidation products derived from the bishydrazone monohydrate of **1** (0–3 mg), dried in a 3-mL, Teflon-capped reacti-vial (Pierce Chemical Co., Rockford, IL 01105) were treated with a solution (0.2 mL) containing hydroxylamine hydrochloride (0.6 g) in anhydrous methanol (2.0 mL) and anhydrous pyridine (4.0 mL), to which was added 1-dimethylamino-2-propanol[10,11] (0.55 mL). The mixture was heated from 15 min to 4 h at 70°, and dried to a syrup with a stream of air. The hexos-2-ulose 1,2-dioximes were converted to the per-*O*-(trimethyl)silyl *O*-(trimethyl)silyloximes by the addition of *N*-trimethylsilylimidazole (0.4 mL) and *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (0.4 mL). Silylation was complete upon dissolution at room temperature (less than 5 min). The hexos-2-ulose 1,2-dioximes derived from the hexos-2-ulose bis(arylhydrazones) and the trioximes derived from the products of periodate oxidation of the bishydrazone monohydrate of **1** were converted to the *O*-trimethylsilyloxime per-*O*-(trimethyl)silylated derivatives by the addition of *N*,*O*-bis(trimethylsilyl)trifluoroacetamide (0.8 mL). Silylation was complete upon dissolution, which required heating at 40° for 2.5 h. Kept under nitrogen, these derivatives were stable for days. D-Glucose was quantitatively determined by conversion to the per-*O*-(trimethyl)silyl *O*-methyloxime derivative by procedures similar to those reported by Mawhinney *et al.*[10,11].

Periodate oxidation of the bis(hydrazone) of **1**. — The amount of periodate consumed was determined by a method similar to that reported by Khym[15]. Material corresponding to the consumption of 1 mol of periodate per mol was prepared by treatment of the bishydrazone monohydrate with periodic acid in 60% aqueous ethanol. To a solution of this compound (109 mg) in 95% ethanol (76 mL) and water (45 mL) was added periodic acid (200 mg), and the solution allowed to stand for 2 h at room temperature in the dark. The solution was placed on a column of Dowex 2 (AcO^-, 200–400 mesh) anion-exchange resin (0.8 × 2.5 cm), prewashed with 60% aqueous ethanol. The column was washed with 60% aqueous ethanol (200 mL), and the washings were evaporated under diminished pressure to give a powder (84 mg). Crystallization from 1:1 (v/v) ethanol–water gave a material having m.p. 140–145°. Conversion to the per-*O*-(trimethyl)silyl *O*-trimethylsilyl-1,2,5-trioxime as described earlier, followed by g.l.c.–m.s. gave the following mass spectrum: m/z (% relative abundance) 463 (12.9), 374 (10.2), 284 (7.6), 218 (46.7), 147 (50.0), 77 (100), 75 (97.5), and 73 (92.3).

Material corresponding to the consumption of 2 mol of periodate per mol was prepared in the following manner: A suspension of the bishydrazone monohydrate of **1** (50 mg) in 0.1M sodium acetate buffer (pH 5.0, 25 mL) containing sodium metaperiodate (260 mg) was stirred for 75 h at 23° in the dark. The suspension was concentrated to 10 mL, the product collected by filtration, washed with water (10 mL) and air dried (29 mg). Conversion to the *O*-trimethylsilyl per-*O*-(trimethyl)silyl 1,2,4-trioxime performed as described earlier, followed by g.l.c.–m.s. gave the following mass spectrum: m/z (% relative abundance) 361 (10.2), 346 (1.7), 272 (11.0), 267 (10.9), 259 (18.2), 156 (16.4), 147 (51.8), 77 (80.9), 74 (83.6), and 73 (100).

*3-Deoxy-*D-erythro-*hexos-2-ulose* **1**. — The methods of Bayne[13] for the preparation of glycos-2-ulose from bishydrazones were used with the following modification: a suspension of the bishydrazone monohydrate of **1** (10 g) in ethanol (300 mL), water (500 mL), acetic acid (3.1 mL), and freshly distilled benzaldehyde (16 mL) was boiled under reflux. Dissolution was complete within 30 min, and the solution remained clear for an additional 30 min at which time benzaldehyde benzoylhydrazone began to precipitate. Reflux was then continued for an additional 1.5 h. With the concurrent addition of water (500 mL), 300 mL of distillate was collected in less than 30 min. The mixture was cooled and filtered, the filtrate neutralized with IRN-78 anion-exchange resin (CO_2^-), and the mixture again filtered. The filtrate was concentrated under diminished pressure (35—40°) to 200 mL, washed with ether (6 × 100 mL), treated with activated charcoal (2 g), filtered, and evaporated under diminished pressure (35–40°) to a thick syrup. This material was dissolved in water (5 mL), and hot 100% ethanol (100 mL), filtered, and stirred with a mixture of Amberlite IR-120 (H^+) and IRN-78 (CO_2^-) ion-exchange resin. The mixture was filtered, and the filtrate concentrated under diminished pressure (30–35°) to 5 mL, frozen, and lyophilized to give an amorphous powder (3.7 g).

Anal. Calc. for $C_6H_{10}O_5 \cdot H_2O$: C, 40.2; H, 6.69. Found: C, 40.2; H, 6.70.

D-arabino-*Hexos-2-ulose* (**2**). — The methods of Richtmyer[16] and Bayne[13] for the preparation of D-*arabino*-hexos-2-ulose bis(phenylhydrazone) and subsequent conversion to the corresponding hexos-2-ulose were used without modification. Recrystallization of D-glucose phenylosazone in 50% aqueous pyridine gave a product having m.p. 204–205° dec. [lit.[16] m.p. 208–209° (dec.)], $[\alpha]_D^{18}$ −58° (6 h)→−39° (126 h) (*c* 0.88; 2:3, v/v, pyridine–ethanol) {lit.[16], $[\alpha]_D^{20}$ −72° (initial)→−40° (48 h) (*c* 0.88; 2:3, v/v, pyridine–ethanol)}. Treatment of the hexos-2-ulose with hydrochloric acid and ethanethiol[13] at 0° gave D-*arabino*-hexos-2-ulose diethyl dithioacetal, m.p. 101–102°; lit.[13] m.p. 101–103°.

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