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STUDIES ON 3-EPIMERIC 2-HEXULOSE PHENYLOSAZONES. STRUCTURE AND ANOMERIC CONFIGURATION OF THE 3,6-ANHYDRO-OSAZONE DERIVATIVES OBTAINED FROM D-*arabino*- AND D-*ribo*-2-HEXULOSE PHENYLOSAZONE*

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ABSTRACT

Dehydration of the 3-epimeric 2-hexulose phenylosazones D-*arabino*-hexulose phenylosazone or D-*ribo*-hexulose phenylosazone afforded 3,6-anhydro-D-*ribo*-hexulose phenylosazone (**4**) as the preponderant isomer from both. The identity of **4** was obtained by t.l.c., and by acylation followed by comparison of the products. Prolonged acetylation with acetic anhydride–pyridine, or by refluxing with acetic anhydride, afforded the same *N*-acetyldi-*O*-acetyl derivative. Refluxing **4** with copper sulfate, or the osotriazole with 20% methanolic sulfuric acid, afforded the *C*-nucleoside analog, namely, 4-β-D-erythrofuranosyl-2-phenyl-1,2,3-osotriazole (**7**). The anomeric configurations of **4** and **7** were ascertained from the n.m.r. spectra of their isopropylidene derivatives. The mechanism of the dehydrative cyclization process and the mass spectra of two compounds were discussed.

INTRODUCTION

Monosaccharide 3,6-anhydro-osazones are compounds of considerable interest as precursors for the synthesis of *C*-nucleosides[2–5]. They are readily prepared by dehydrative cyclization of the polyhydroxyalkyl chain of monosaccharide phenylosazones with methanolic sulfuric acid solution. The dehydrative cyclization of monosaccharide phenylosazones, and of the monosaccharide heterocyclic analogs[6–9] in general, is a stereospecific process accompanied by inversion at the carbon atom α to the heterocyclic base, which makes the assignment of the anomeric configuration of the products of significant importance. Circular dichroism[10] and high-resolution n.m.r. spectroscopy[11] were used for this purpose.

The dehydrative cyclization process is controlled by different factors. (*a*) The length of the polyhydroxyalkyl chain; recent studies on hexulose[11] and heptulose

*Studies on Anhydro-osazones, Part IV. For Part III, see ref. 1.
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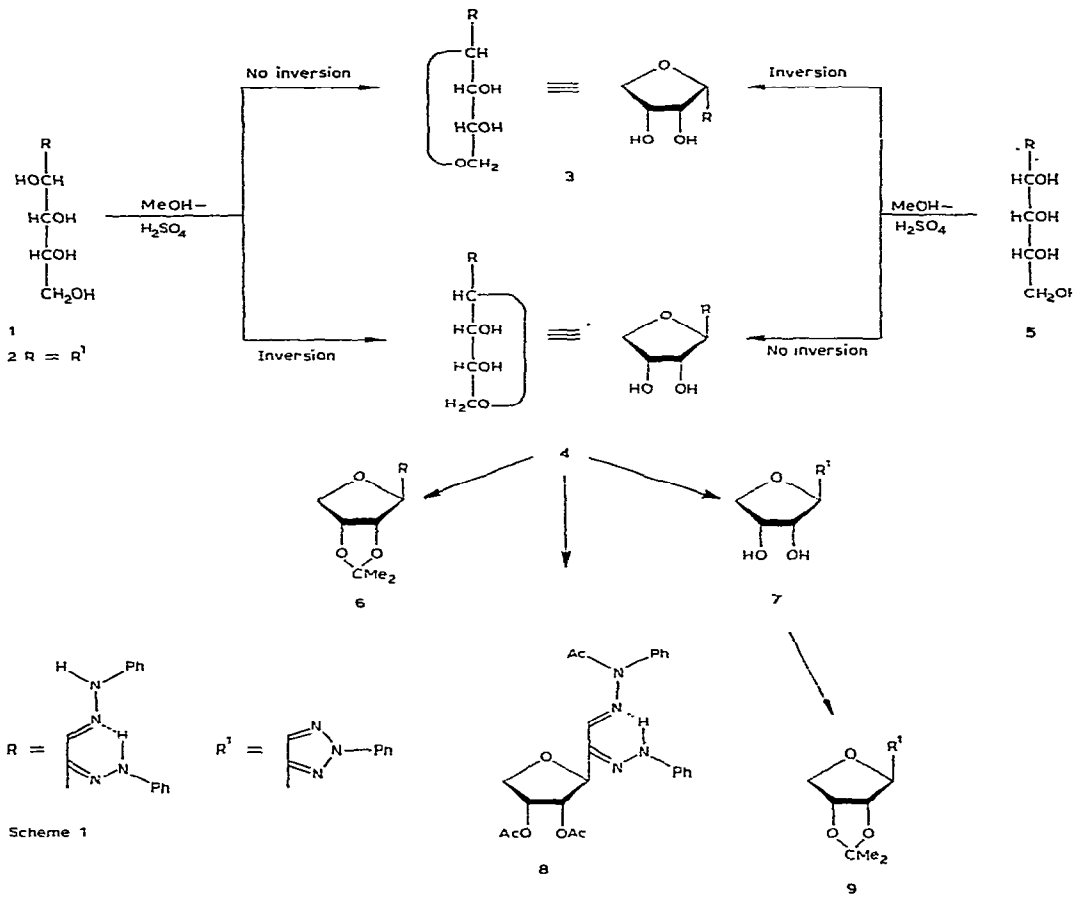
phenylosazones[12] indicated that the dehydrative cyclization process is more stereospecific for the hexulose analogs. (*b*) The relative configuration of the hydroxyl groups α and β to the heterocyclic base; studies based on c.d. measurements indicated[10] that atom C-3 of the 3,6-anhydro-osazone formed tends to have the same configuration as C-4 in the Fischer projection-formula, irrespective of the configuration of C-3 in the starting osazone. Recently[11,12], it was found that this is restricted only for the hexulose analogs. (*c*) The bulkiness of the base; for polyhydroxyalkyl, heterocyclic analogs having the same length of the polyhydroxyalkyl chain, the bulkier the base the more stereospecific the process. Monosaccharide pyrazolo[3,4-*b*]quinoxalines[13] produce only one isomer having a trans relationship between the base moiety and the 2-hydroxyl group. Hexulose phenylosazones[11], triazoles[14,15], and pentahydroxypentylfurans[8,16] produce two isomers, the isomer having a *trans* relationship between the 2-hydroxyl group and the base moiety preponderating. A mechanism was suggested by El Khadem[17] for explaining the stereospecifity of the dehydration of hexulose phenylosazones, and this was supported recently[11] by n.m.r.-spectral studies, and by studies on 3-epimeric hexulose phenylosazones[18]. The present work describes the dehydration of another pair of 3-epimeric hexulose phenylosazones, namely, D-*arabino*-2-hexulose phenylosazone and D-*ribo*-2-hexulose phenylosazone, with methanolic sulfuric acid solution, and the identity of the products was ascertained by t.l.c. and by acetylation. The anomeric configuration of the products was determined by n.m.r. spectroscopy.

DISCUSSION

Dehydration of D-*arabino*-2-hexulose phenylosazone (**1**) by refluxing with methanolic sulfuric acid solution, with monitoring of the reaction by t.l.c., afforded 3,6-anhydro-D-*ribo*-hexulose phenylosazone (**4**) as the preponderant product. Compound **4** is formed from **1** by inversion in the configuration of C-3 (C-1 of the aldosyl group formed; see Scheme 1). Its n.m.r. spectrum showed the anomeric proton as a doublet at δ 4.67 ($J_{1',2'}$ 6.3 Hz). This value of the coupling constant makes the anomeric assignment of compound **4** uncertain[19,20], as it agrees with either a *cis* or *trans* arrangement for H-1′ and H-2′ of the D-erythrofuranosyl group formed. Excluding conformational changes, the *trans* assignment of the anomeric proton on the basis of the observed coupling constant is certain[19,21] only if the coupling constant ($J_{1',2'}$) for the anomeric proton is less than 3.5 Hz. Acetylation of **4** by refluxing with acetic anhydride, or by treatment with acetic anhydride–pyridine for 7 days, afforded the *N*-acetyl-di-*O*-acetyl derivative **8**. Its i.r. spectrum showed bands at 1755 and 1695 cm^{-1}, due to the *O*-acetyl and *N*-acetyl groups, respectively. Additionally, the n.m.r. spectrum of **2** showed two *O*-acetyl groups as two singlets, each of three-proton intensity, at δ 2.00 and 2.03, and the *N*-acetyl group as a broad singlet at δ 2.42. The anomeric proton of **8** appeared as a doublet at δ 4.45 ($J_{1',2'}$ 6.0 Hz), but this value of the coupling constant for **8** cannot decide the anomeric configuration. However, the n.m.r. spectrum of the isopropylidene derivative **6** (see Fig. 1) showed the



anomeric proton as a doublet at δ 4.32 ($J_{1',2'}$ 3.61 Hz); the small value of $J_{1',2'}$ observed for **6** is in close agreement with the β-D-*erythro* configuration.

Additional evidence for the β-D configuration was obtained from the difference ($\Delta\delta$) between the chemical shifts of the methyl signals of the 2,2-dimethyldioxolane ring; the difference of 0.222 (1.545 — 1.323) between the chemical shifts of the two methyl protons of **6** is consistent[22–25] with the β-D-*erythro* configuration. The n.m.r.-spectral assignment for compound **6** supports the β-D-*erythro* configuration for compound **4** (which is obtained from **1** with inversion in the configuration of C-3). This n.m.r.-spectral assignment is in agreement with the observed[10] Cotton effect in the c.d. spectrum of compound **4**. The minor isomer **3**, which is formed from **1** without inversion in the configuration, and was detected[14] in small proportion, could also be detected, by t.l.c. using different solvent mixtures, in small proportion in the mother liquor, and was tentatively assigned the α-D-*erythro* configuration.

On being refluxed with copper sulfate, compound **4** afforded the *C*-nucleoside derivative, namely, 4-β-D-erythrofuranosyl-2-phenyl-1,2,3-osotriazole (**7**), in 30% yield. Its n.m.r. spectrum showed the anomeric proton at δ 4.97 ($J_{1',2'}$ 6.1 Hz), but

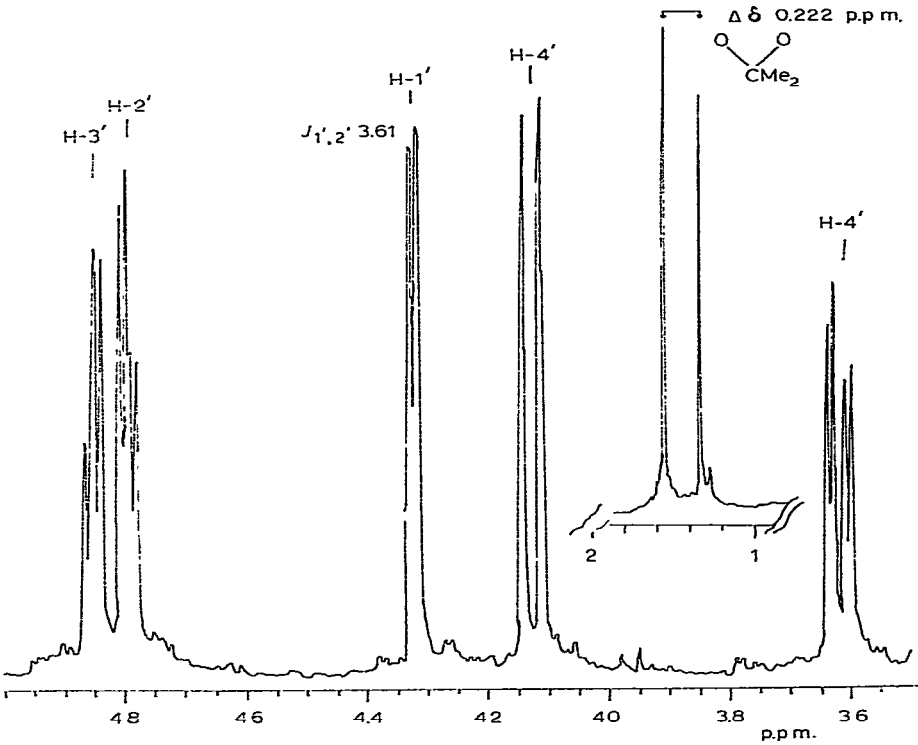


Fig. 1. N.m.r. spectrum, at 360 MHz, of 4,5-*O*-isopropylidene-β-D-*erythro*-hexulofuranose bis(phenylhydrazone) (6) + CD_3CO_2D (high resolution for the sugar moiety).

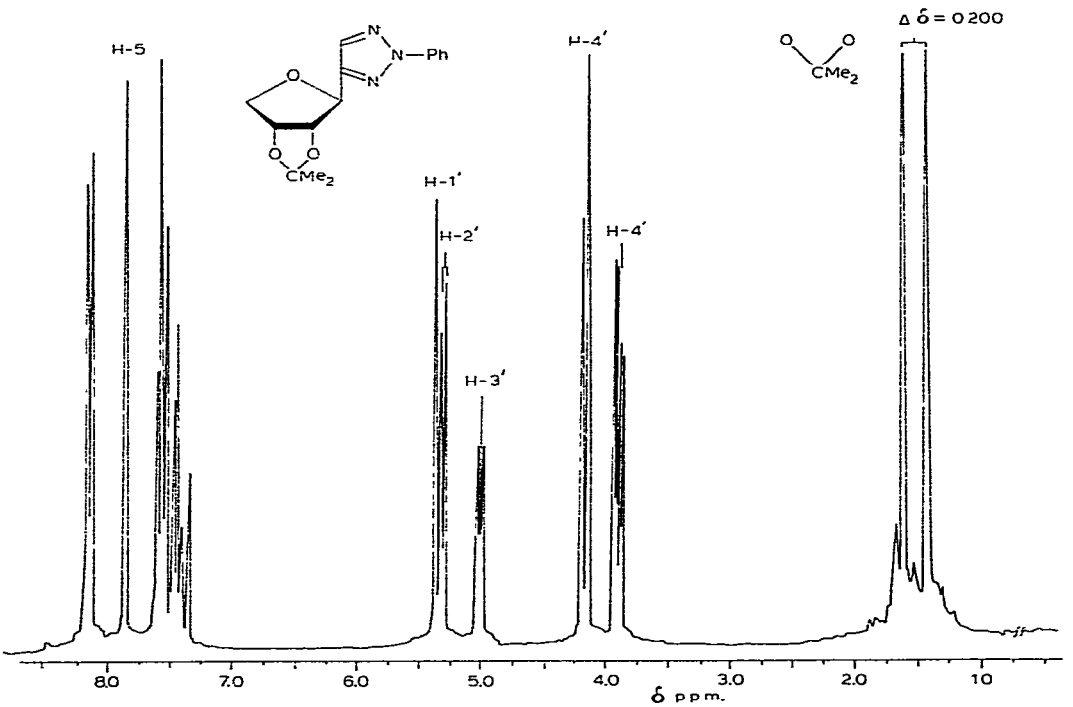


Fig. 2. N.m.r. spectrum, at 270 MHz, of 4-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-phenyl-1,2,3-osotriazole (9).

this value of the coupling constant could not be used to ascertain the anomeric configuration. However, the n.m.r. spectrum of the isopropylidene derivative **9** (see Fig. 2), showed the anomeric proton as a singlet at δ 5.33. The observed zero value of the coupling constant for the anomeric proton of **9** proved unequivocally[19,21,26] the trans arrangement of H-1′ and H-2′, that is, the *β*-D-*erythro* configuration. Dehydration of D-*arabino*-hexulose phenylosotriazole (**2**) with 20% methanolic sulfuric acid afforded compound **7** in higher yield (59%).

In order to investigate the steric course of the dehydration of **1**, the 3-epimeric D-*ribo*-hexulose phenylosazone (**5**) was similarly dehydrated with methanolic sulfuric acid solution (with monitoring of the reaction by t.l.c.), and the products obtained were compared with those from compound **1**. Dehydration of **5** afforded the same 3,6-anhydro-osazones as had been obtained from **1**, having the same mobility in t.l.c. using different solvent mixtures (*A*, *B*, and *C*), and compound **4** was also obtained as the preponderant isomer from **5**. Acetylation with acetic anhydride–pyridine for 7 days, or by refluxing with acetic anhydride, afforded the same *N*-acetyldi-*O*-acetyl derivative (**8**), having the same melting point and mixed-melting point.

The formation of two isomers (major and minor) from the two 3-epimeric saccharide phenylosazones **1** and **5**, indicates that racemization took place at C-3 at a certain stage of the reaction, with the formation of the same intermediate. This intermediate may be the 2-(phenylazo)-2-ene intermediate suggested by Simon and co-workers[27,28] and El Khadem[17]. Although such an alkenic intermediate has not been isolated from the dehydration reaction, several 2-ene intermediates have been shown to be formed in the course of osazone reactions[28], and it is in accord with the observation[4] that D-glucose alkylphenylosazones cannot be converted into anhydro-osazones. The formation of a carbonium-ion intermediate analogous to the one suggested for the dehydration of polyhydroxyalkylfurans[16] is rather less predictable than the 2-ene alkenic intermediate of the anhydro-osazones, for the following reasons. *a*. The carbonium-ion intermediate is thermodynamically less stable than the 2-phenylazo-2-ene intermediate. *b*. The formation of the latter is more facilitated[17] by the presence of the *β* imino proton of the 2-hydrazone residue. *c*. Refluxing of a pure sample of **4** in methanolic sulfuric acid solution (with monitoring of the reaction by t.l.c.) did not produce spots at the R_F value of the precursor osazones **1** or **5**, as would be expected for the carbonium-ion intermediate. This may be attributed

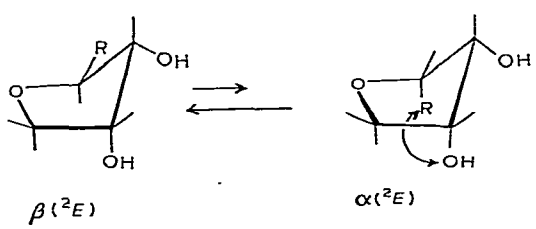


Fig. 3. The preponderant conformers of anomeric D-erythrofuranosyl bis(phenylhydrazone).

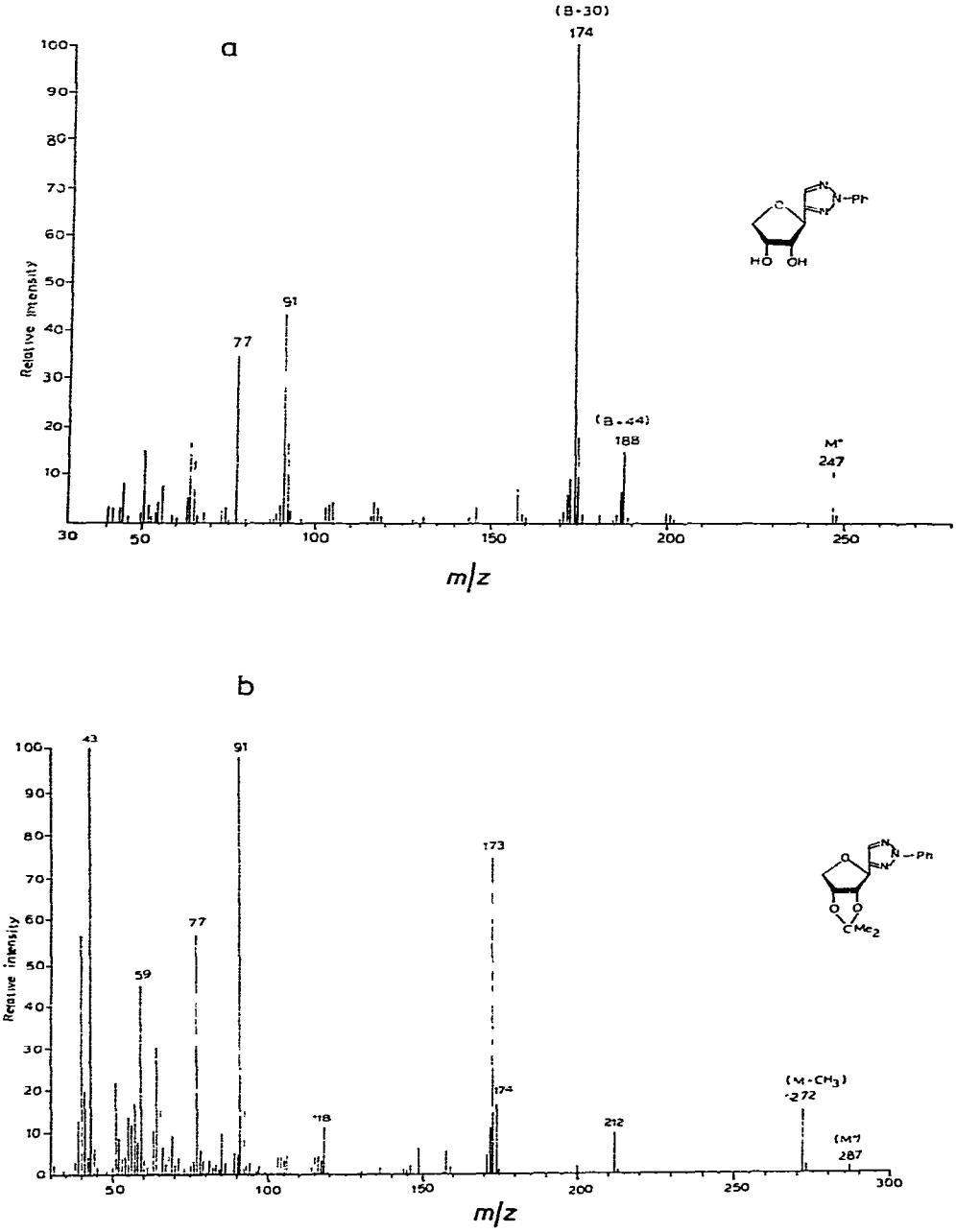
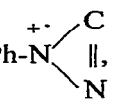


Fig. 4. Mass spectrum of (a) 4-β-D-erythrofuranosyl-2-phenyl-1,2,3-osotriazole; (b) 4-(2,3-*O*-isopropylidene-β-D-erythrofuranosyl)-2-phenyl-1,2,3-osotriazole.

to the stability of the furanose ring formed, which does not revert to the acyclic compounds **1** and **5** under the reaction conditions.

The formation of compound **4** as the preponderant isomer (with inversion from **1**, and without inversion from **5**) further illustrates the stereospecificity of the dehydration process, and supports the mechanism suggested by El Khadem[17] for the dehydration of hexulose phenylosazones. The preponderant isomer **4** has a *trans* relationship between the bis(hydrazone) residue and the 2-hydroxyl group in the Haworth formula of the glycosyl group formed; the minor isomer (**3**) has a *cis* relationship. The preponderance of **4** over **3** may also be explained by its higher conformational stability. The ^{2}E conformer of compound **3** (see Fig. 3) is less stable, due to the *syn*-axial interaction between the bulky, axially attached bis(hydrazone) residue and the 3-hydroxyl group. This may explain the general production of 3,6-anhydro-saccharide heterocyclic derivatives preferentially having the *ribo* configuration upon dehydration of their precursors, D-*arabino* heterocyclic analogs[8,16].

The mass spectrum of compound **7** (see Fig. 4a) showed the molecular-ion peaks, M and M + 1, at *m/z* 247 and 248, respectively. The peak (B + 30) characteristic for *C*-nucleosides was shown as a base peak at *m/z* 174, confirming the carbon–carbon linkage between the erythrofuranosyl group and the base moiety. The peak (B + 44), which is also abundant for higher homomorphous *C*-nucleoside osotriazole analogs[1], was shown at *m/z* 188, indicating an identical type of fragmentation. However, the mass spectrum of the isopropylidene derivative **9** (see Fig. 4b) showed a low-intensity molecular-ion at *m/z* 287, which was followed by a peak at *m/z* 272 corresponding to a cyclic acetate fragment obtained by the loss of $CH_3^{\cdot}$ from the molecular ion. This was followed by a peak at *m/z* 212 corresponding to the loss of acetic acid from the cyclic acetate fragment. The peaks characteristic of *C*-nucleosides. BHCHO and BHCO, were shown at *m/z* 174 and 173, respectively, but with different intensity than for the precursor *C*-nucleoside **7**. The peaks at *m/z* 118 corresponding to the cyclic cation  , and at *m/z* 91 corresponding to PhN, were obtained by the loss of HCN and decomposition of the base moiety. The base peak was shown at *m/z* 43, corresponding to the CH_3CO group.

EXPERIMENTAL

General. — Melting points were determined with a Fisher–Johns melting-point apparatus and are uncorrected. Evaporations were performed under diminished pressure below 60°. Thin-layer chromatography (t.l.c.) was conducted on silica gel (Kiesel gel G, Merck) with solvent *A*, 3:1 benzene–ethanol; solvent *B*, 2:1:1 benzene–chloroform–ethanol; and solvent *C*, 4:1:1 benzene–petroleum ether–ethanol. Optical rotations were measured at 20 ±2° with a Perkin–Elmer 141 polarimeter (10-cm, 1-mL microcell). I.r. absorption spectra were recorded with a Unicam SP 1025 and a Perkin–Elmer 337 instrument, and u.v. absorption spectra with a

Beckman 125 spectrophotometer. N.m.r. spectra were recorded with Varian T (60 MHz), Bruker WH (270 MHz), NTC (360 MHz), or NTC (470 MHz) instruments, using internal tetramethylsilane as the standard. Mass spectra were recorded with a Finnigan 6100 Data System Gas-Chromatograph/EI-CI spectrometer. Combustion analyses were performed in the Department of Chemistry, Faculty of Science, Cairo University, Cairo, Egypt, and the Department of Chemistry, Purdue University, W. Lafayette, IN, U.S.A.

3,6-Anhydro-D-ribo-*hexulose phenylosazone* (**4**). — *Method 1. From* D-arabino-*hexulose phenylosazone* [D-*glucose phenylosazone* (**1**)]. Compound **1** (4 g) was boiled for 6 h under reflux with methanolic sulfuric acid (made by adding 0.3 mL of conc. sulfuric acid and 1.2 mL of water to 600 mL of methanol); t.l.c. (solvent *A*) then revealed the absence of the starting osazone and formation of two spots (in the ratio of ~5:1, respectively) having R_F 0.60, 0.67 (solvent *A*), 0.45, 0.52 (solvent *B*), and 0.52, 0.59 (solvent *C*). The solution was diluted with hot water (250 mL), and the methanol was evaporated under diminished pressure. The precipitate obtained was filtered off, washed with water, and dried; yield 2.5 g. The mixture was purified by chromatography on a column (3 × 60 cm) of silica gel, with solvent *A* as the eluant. The fractions were combined, and, on concentration, gave yellow needles of **4**. It was recrystallized from dilute methanol, to give chromatographically (t.l.c.) pure, yellow needles, m.p. 178–179° (lit.[14] m.p. 179–180°), $[\alpha]_D^{22}$ −130° (*c* 1.1, acetone) {lit.[14] $[\alpha]_D$ −150° (*c* 0.6, methanol)}; R_F (the slower-moving spot) 0.60 (solvent *A*), 0.45 (solvent *B*); n.m.r. data (270 MHz, Me_2SO-d_6): δ 3.79–3.82 (dd, 1 H, H-4), 4.17–4.23 (m, 2 H, H-4′, OH), 4.25–4.33 (bs, 2 H, H-2′,3′), 4.36 (bs, 1 H, OH), 4.42 (d, 1 H, H-1′), 6.82–7.50 (m, 10 H, aromatic protons), 7.75 (s, 1 H, aldimino proton), 9.85 (s, 1 H, nonchelated NH of C-1 hydrazone residue), and 12.40 (s, 1 H, chelated NH of C-2 hydrazone residue); after addition of CD_3CO_2D, the two NH and the two OH protons disappeared: δ 3.79–3.82 (dd, 1 H, H-4″, $J_{3',4''}$ 2.0, $J_{4',4''}$ 9.7 Hz), 4.15–4.19 (dd, 1 H, H-4′, $J_{3',4'}$ 3.7 Hz), 4.36–4.37 (bd, 2 H, H-2′,3′, $J_{2',3'}$ 4.2 Hz), and 4.47 (d, 1 H, H-1′, $J_{1',2'}$ 6.3 Hz).

Method 2. From D-ribo-*hexulose phenylosazone* (**5**). Compound **5** (5 g, prepared from the mixture of the 2-epimeric hexoses, D-allose and D-altrose, obtained from D-ribose cyanohydrin[29]) was boiled for 6 h under reflux with methanolic sulfuric acid (400 mL), the reaction being monitored by t.l.c.; after 4 h, t.l.c. (solvent *A*) revealed the formation of two spots similar to those obtained by method 1, at the same R_F values (solvents *A* and *B*). The solution was processed as described for compound **1**; yield 3.5 g. It was purified by column chromatography with solvent *A* as the eluant; the yellow fractions were combined, and evaporated to dryness, and the residue was recrystallized from methanol, to give chromatographically pure (t.l.c.) needles, m.p. and mixed m.p. (with **4**) 179–180°, having the same R_F values (solvents *A*, *B*, and *C*).

On boiling a sample of **4** with methanolic sulfuric acid for 8 h, monitoring of the reaction by t.l.c. did not show the formation of spots at the R_F value of **1** or **5**.

The minor isomer (**3**) was detected in the mother liquor (method 1 and 2), by

t.l.c. using solvent mixtures *A*, *B*, and *C*, at R_F 0.67, 0.52, and 0.59, respectively, as a faster-moving, faint spot.

N-*Acetyl-2,3-di*-O-*acetyl-3,6-anhydro*-D-ribo-*hexulose phenylosazone* (**8**). — Compound **4** (method 1, 2 g) was treated with 1 : 1 acetic anhydride–pyridine (20 mL) for 7 days at room temperature, poured onto crushed ice, and the precipitate filtered off, washed with water, and dried; yield 2.0 g. It was recrystallized from methanol, to give yellow needles of **8**, m.p. 174–176°; ν_{max}^{KBr} 1755 (OAc), 1695 (NAc), and 1600 cm^{-1} (C=N); n.m.r. data (60 MHz, $CDCl_3$): δ 2.0 and 2.03 (d, 6 H, 2 CH_3CO), 2.42 (bs, 3 H, *N*-$COCH_3$), 3.65–4.00 (m, 2 H, H-4′,4″), 4.44 (s, 1 H, H-1′, $J_{1',2'}$ 6.0 Hz), 5.25–5.48 (m, H, H-2′,3′), 6.80–7.55 (m, 10 H, aromatic protons), and 12.40 (bs, 1 H, NH).

Anal. Calc. for $C_{24}H_{26}N_4O_6$: C, 61.80; H, 5.62; N, 12.01. Found: C, 61.40; H, 5.90; N, 11.57.

Compound **4** (method 1), on being refluxed with acetic anhydride for 1 h and processed as described before, gave compound **8**, m.p. and mixed m.p. 176–178°.

Compound **4** (method 2), by similar treatment with 1 : 1 acetic anhydride–pyridine for 7 days, and processing as described before, afforded yellow needles, m.p. and mixed m.p. with **8** (method 1), 176–178°.

4,5-O-*Isopropylidene*-*β*-D-erythro-*hexulofuranose bis*(*phenylhydrazone*) (**6**). — A solution of compound **4** (60 mg) in dry acetone (50 mL) was treated with *p*-toluenesulfonic acid (300 mg) with stirring for 15 h, poured into an ice-cold, saturated solution of sodium hydrogencarbonate, and the resulting precipitate filtered off, washed with water, and dried; yield 75 mg. It was recrystallized from dilute methanol, to give yellow needles, m.p. 227–229°; t.l.c. (solvent *A*), R_F 0.82; n.m.r. data (360 MHz, $CDCl_3$): δ 1.325 and 1.544 (d, 6 H, CMe_2, $\Delta\delta$ 0.221), 3.60–3.64 (dd, 1 H, H-4′, $J_{3',4'}$ 3.7 Hz), 4.11–4.14 (d, 1 H, H-4′, $J_{4',4''}$ 10.7 Hz), 4.32 (d, 1 H, H-1′, $J_{1',2'}$ 3.61 Hz), 4.78–4.81 (dd, 1 H, H-2′, $J_{2',3'}$ 5.5 Hz), 4.84–4.87 (t, 1 H, H-3′), 6.90–7.37 (m, 10 H, aromatic protons), 7.67 (s, 1 H, aldimino proton), and 12.39 (s, 1 H, chelated NH of C-2 hydrazone residue).

Anal. Calc. for $C_{21}H_{24}N_4O_3$: C, 66.30; H, 6.35; N, 14.73. Found: C, 66.61; H, 6.56; N, 14.90.

4-β-D-*Erythrofuranosyl-2-phenyl-1,2,3-osotriazole* (**7**). — *Method 1. From 3,6-anhydro*-D-ribo-*hexulose phenylosazone* **4**. A suspension of compound **4** (2 g) in water (100 mL) was boiled under reflux, with stirring, and a solution of copper sulfate (2 g) in water (50 mL) was added dropwise; then, 1-propanol (4 mL) was added, and the mixture was boiled for 6 h. It was cooled, filtered, and the filtrate freed of copper sulfate by bubbling H_2S gas through it, filtering the suspension, and then stirring the filtrate with barium carbonate, and filtering. The filtrate was stirred with Amberlite IR-MB cation–anion-exchange resin, and the resin was filtered off, and washed thoroughly with methanol; the filtrate and washings were combined, and evaporated to a syrup which crystallized from benzene, to give colorless needles; yield 0.6 g (30%), m.p. 80–82° (lit.[14] m.p. 80–83°): $[\alpha]_D^{20}$ −71.8° (*c* 1.9, methanol): R_F 0.75 (*A*), 0.50 (*B*), and 0.51 (*C*); ν_{max}^{KBr} 3250 (OH), 1590 (C=N), and 1455, 750

cm^{-1} (Ph); λ_{max}^{MeOH} 266 nm (log ε 4.3); n.m.r. data (470 MHz, $CDCl_3$): δ 3.63 (bs, 1 H, OH), 3.83 (bs, 1 H, OH), 3.90–3.93 (dd, 1 H, H-4″, $J_{3',4'}$ 3 Hz), 4.22–4.25 (dd, 1 H, H-4′, $J_{3',4'}$ 5, $J_{4',4''}$ 10 Hz), 4.34–4.39 (m, 2 H, H-2′,3′), 4.97 (d, 1 H, H-1′, $J_{1',2'}$ 6.1 Hz), 7.30–7.44 (m, 3 H, meta and para protons of the phenyl group), 7.76 (1 H, H-5), and 7.98–7.99 (d, 2 H, ortho protons of the phenyl group). After addition of CD_3CO_2D, the two OH protons disappeared.

Method 2. From D-*glucose phenylosotriazole* (**2**). A suspension of compound **2** (29 g) in methanol (200 mL) was mixed with concentrated sulfuric acid (40 mL), and the mixture was boiled under reflux for 8 h on a boiling-water bath. It was cooled, diluted with water, the methanol evaporated under diminished pressure, and the solution extracted with chloroform (3 × 200 mL). The extracts were combined, successively washed with water, sodium hydrogencarbonate, and water, dried (anhydrous sodium sulfate), and evaporated, to afford colorless needles; yield 15.8 (59%). It was recrystallized from benzene, m.p. and mixed m.p. 82–84°.

*4-(2,3-*O*-Isopropylidene-β-*D*-erythrofuranosyl)-2-phenyl-1,2,3-osotriazole* (**9**). — A solution of **7** (300 mg) and *p*-toluenesulfonic acid (500 mg) in dry acetone (50 mL) was stirred overnight at room temperature. T.l.c. (solvent *A*) then indicated the absence of compound **7** and formation of a more-mobile spot, R_F 0.86. The mixture was poured into an ice-cold solution of sodium hydrogencarbonate, and extracted with chloroform. The extract was washed with water, dried (anhydrous sodium sulfate), and evaporated to a syrup which crystallized from dilute methanol, giving **9** as colorless needles, yield 279 mg; m.p. 62°, $[\alpha]_D^{20}$ −40.2° (*c* 1.2, methanol); ν_{max}^{KBr} 1595 (C=N), 1498, 1350 (CMe_2) and 750 cm^{-1} (Ph); λ_{max}^{MeOH} 266 nm (log ε 4.3); n.m.r. data (270 MHz, $CDCl_3$): δ 1.396 and 1.596 (d, 6 H, CMe_2, Δδ 0.200), 3.84–3.90 (dd, 1 H, H-4″, $J_{3',4''}$ 3.8, $J_{4',4''}$ 11.3 Hz), 4.11–4.15 (d, 1 H, H-4′, $J_{3',4'}$ 0, $J_{4',4''}$ 11.3 Hz), 4.95–4.99 (t, 1 H, H-3′), 5.27 (d, 1 H, H-2′, $J_{2',3'}$ 6.7 Hz), 5.33 (s, 1 H, H-1′), 7.33–7.81 (m, 3 H, meta and para protons of the phenyl group), 7.81 (s, 1 H, H-5), and 8.00–8.19 (d, 2 H, ortho protons of the phenyl group).

Anal. Calc. for $C_{15}H_{17}N_3O_3$: C, 62.71; H, 5.96; N, 14.61. Found: C, 62.73; H, 5.74: N, 14.46.

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