# Studies on Anhydro-osazones. Part 5.[1] Structure and Anomeric Configuration of the *C*-Nucleoside Analogues Obtained from the Dehydration of D-*gluco*- and D-*manno*-Hept-2-ulose Phenylosazones

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Dehydration of D-*gluco*- and D-*manno*-hept-2-ulose phenylosazones with methanolic sulphuric acid afforded the anomeric furanosyl anydro-osazone pair: 3,6-anhydro-D-*manno*-hept-2-ulose phenylosazone (2), and the *gluco*-analogue osazone (3). A new type of anomeric pyranosyl anhdro-osazone [3,7-anhydro-D-*manno*-hept-2-ulose phenylosazone (4) and the *gluco*-analogue (5)] was also identified. Refluxing the anhydro-osazones with copper sulphate afforded the anomeric furanosyl *C*-nucleoside analogues 4-α-D-arabinofuranosyl-2-phenyl-*v*-triazole (6) and the β-isomer (7), and the arabinopyranosyl isomers (8) and (9). The structures and anomeric configurations of the products were determined by periodiate oxidation, o.r.d., and n.m.r. spectroscopy. The mechanism of the dehydration and the mass spectra of compounds (6)—(9) are discussed.

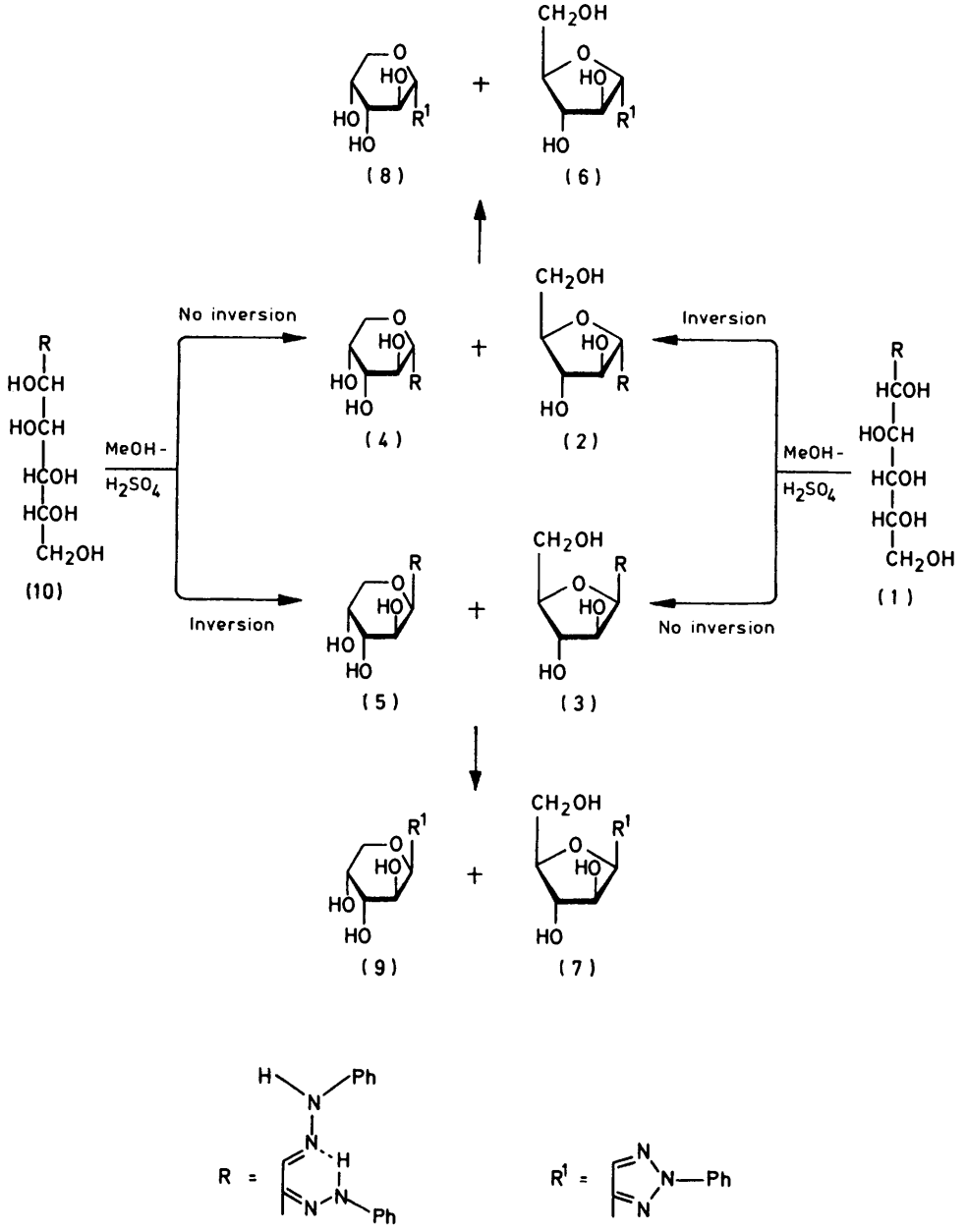
ANHYDRO-OSAZONES are of interest [2-6] as precursors of *C*-nucleoside analogues because of their ease of dehydration, giving a wide variety of *C*-glycosyl moieties, especially those having rare configurations which cannot be obtained readily by simple synthetic methods. The carbon–carbon linkage between the glycosyl part and the base moiety of *C*-nucleosides is more stable [7] towards acidic and enzymic hydrolysis than the carbon–nitrogen linkage of *N*-nucleosides which makes the former useful tools for biochemical investigations. Anhydro-osazones are readily prepared by dehydrative cyclization of the polyhydroxyalkyl chain of saccharide osazones with methanolic sulphuric acid. Hexose phenylosazones give 3,6-anhydro-derivatives and the dehydration is accompanied by inversion at the carbon atom α to the bis-(hydrazone) residue. The inversion can be detected by circular dichroism [8] or more conveniently by n.m.r. spectroscopy.[9] Recent studies [1,10] on 3-epimeric hexulose phenylosazones have indicated that the dehydration process is stereoselective, giving preponderantly the isomer having a *trans*-relationship between the bis-(hydrazone) residue and the 4-hydroxy-group (2-OH of the aldosyl group formed). A mechanism for this process was suggested by El Khadem [11] and supported by studies [1,10] on 3-epimeric hexulose phenylosazones, and by n.m.r. spectroscopy.[9] The dehydration of higher monosaccharide phenylasazones [12,13] did not show the same general correlation: the dehydration process differs from one higher sugar phenylosazone to another according to the configuration of the polyhydroxylalkyl chain. In the present work the dehydration of the 3-epimeric D-*manno*- and D-*gluco*-hept-2-ulose phenylosazones with methanolic sulphuric acid has been studied. Two anomeric pairs of osazones (3,6-anhydro- and 3,7-anhydro-) were identified, and were converted into the corresponding triazole *C*-nucleoside analogues.

Dehydration of D-*gluco*-hept-2-ulose phenylosazone (1) by refluxing with methanolic sulphuric acid (with monitoring of the reaction by t.l.c.) afforded four isomeric anhydro-osazones (2)—(5). Anhydro-osazone isomers are difficult to separate because of their identical solubility properties and their close $R_F$ values. In addition, their n.m.r. spectra show overlapping of the sugar proton signals and their c.d. spectra in some cases [12] contradict the results from n.m.r. spectroscopy. Thus compounds (2)—(5) were only partially separated by t.l.c.; however, the isomers (2) and (5) showed different $R_F$ values, which facilitated their separation.

Refluxing the anhydro-osazone mixture with copper sulphate and subsequent chromatography of the resulting triazole *C*-nucleoside analogues (6)—(9) on ion exchange resin [14] with gradient elution with aqueous methanol resulted in clean separation of the isomers; the pyranosyl analogues were eluted before the furanosyl analogues.

The formation of four isomeric anhydro-osazones (as kinetically controlled products) can be explained in terms of cyclization of the polyhydroxyalkyl chain giving both five membered 3,6-anhydro-osazones (2) and (3) and six-membered 3,7-anhydro-osazones (4) and (5). The latter represent a new type of anhydro-osazone, all previously reported anhydro-osazones having the furanosyl ring structure. The ring size was determined by periodate oxidation of the triazole *C*-nucleoside analogues. Compounds (6) and (7) consumed 1 mol equiv. of periodate, and compounds (8) and (9) 2 mol equiv.

The formation of an anomeric pair in each case can be explained by inversion at C-3 of the starting osazone (C-1 of the furanosyl group formed). The anomeric configurations of the furanosyl derivatives (6) and (7) were determined by n.m.r. spectroscopy. Compound (6) showed a doublet at δ 5.19 ($J_{1',2'}$ 3.7 Hz) in agreement [15] with the *trans* arrangement of H-1′ and H′-2, *i.e.* the α-D-arabinofuranosyl configuration. Compound 7 showed a doublet at δ 4.87 with a larger coupling ($J_{1',2'}$ 6.3 Hz) in accord [15] with a *cis*-arrangement (the β-D-arabinofuranosyl configuration). The anomeric configurations of compounds (6) and (7) were not reflected in the chemical shifts [16-18] of the anomeric protons, as in other *C*-nucleosides where the anomeric proton signal of the *cis*-anomer usually appears at lower field than that of the *trans*-anomer. Compounds (6) and (7) showed the opposite correlation, which is a general feature of triazole *C*-nucleoside analogues. However, the anomeric configuration was confirmed [19] by the chemical shift of H-5




of the triazole moieties; the β-anomer (7) showed H-5 at lower field (δ 8.09) than the α-anomer (6) (δ 7.99) (see Table 1).

Support for the anomeric configurations of (6) and (7) was obtained from their chiroptical properties. Compound (6) showed a larger positive specific rotation ($[\alpha]_D^{22}$ in methanol: (6) + 86.1; (7) +23.7°) in agreement with Hudson's isorotation rule.[20] However, in their o.r.d. spectra (see Figure), they showed plain Cotton effects, and compound (6) exhibited a more positive Cotton effect than (7).

The structures and anomeric configurations of the asazones of (2) and (3) were determined by correlation with the *C*-nucleoside derivatives (6) and (7). In addition, the n.m.r. spectrum of compound (2) (see Table 2) showed the anomeric proton signal as a singlet at δ 4.47, in agreement with the 1′,2′-*trans*-arrangement of the α-D-arabinofuranosyl group. The high specific rotation $[\alpha]_D$ +110° of (2) supports the α-D-configuration. The n.m.r. spectrum of compound (3) showed the anomeric proton signal as a doublet at δ 4.49 ($J_{1',2'}$ 6.8 Hz) in agreement[15] with the 1,′2′-*cis*-arrangement of the β-D-arabinofuranosyl group.

The n.m.r. spectra of the pyranosyltriazoles (8) and (9) showed the anomeric proton signals as a singlet at δ 4.94 and a doublet at δ 4.26 ($J_{1',2'}$ 9.6 Hz), respectively. The assignment of anomeric configuration from the coupling constant ($J_{1',2'}$), although valuable for furanosyl

nucleosides, is in many cases unsuitable for pyranosyl analogues,[17,21-23] because of the possibility of conformational isomerism. However applying the criterion [19] of the H-5 chemical shift [δ 8.03 for (9); δ 7.99 for (8)] supports the β-configuration for (9) and the α-configuration for (8). This was confirmed by their chiroptical properties: compound (9) showed negative specific rotation ($[\alpha]_D^{22}$ −56.5°) and (8) showed positive rotation ($[\alpha]_D^{20}$ +66.2°) in accord with Hudson's rules.[20] In their o.r.d. spectra (see Figure), compound (8) showed a positive plain Cotton effect [identical with that of the closely related α-furanosyl analogue (6)] and compound (9) a negative plain Cotton effect in the same wavelength region, supporting the anomeric assignment from n.m.r. spectroscopy.

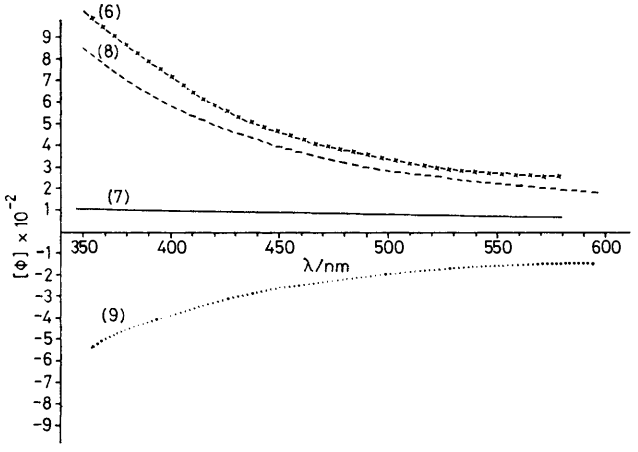



FIGURE O.r.d. spectra of the triazoles (6)—(9)

The structures and anomeric configurations of the 3,7-anhydro-osazones (4) and (5) were determined by correlation with the triazole *C*-nucleosides (8) and (9). In addition, the n.m.r. spectrum of (5) showed the anomeric proton signal as a doublet at δ 4.00 ($J_{1',2'}$ 9.1 Hz), and the α-configuration was indicated by the negative specific rotation ($[\alpha]_D^{22}$ −27.8°). The previously [6] reported 3,6-anhydro-osazone, isolated from the mixture by crystallization, was the isomer (2).

In order to shed some light on the stereochemical course of the dehydrative cyclization of D-*gluco*-hept-2-ulose phenylosazone (1), the 3-epimeric D-*manno*-hept-2-ulose phenylosazone (10), was similarly dehydrated. The same anhydro-osazones (2)—(5) were obtained with little change in proportions (t.l.c.). Refluxing the anhydro-osazone mixture with copper sulphate and separation by ion-exchange column chromatography afforded the same *C*-nucleoside anomeric pairs [(6), (7) and (8), (9)]. This indicates that both compounds (1) and (10) undergo inversion at C-3. The isolation of the same anomeric pairs in appreciable proportions from both (1) and (10) indicates a less stereoselective dehydration than for the analogous hexulose phenylosazones. In addition, it indicates the formation of a common intermediate, incompatible with a simple $S_N2$ mechanism. The racemization at C-3 can be explained by the formation of a carbocation intermediate, similar to that suggested for the cyclization of 2-(D-*arabino*-tetrahydroxybutyl)furans.[24] Boiling a pure sample of (5) or (2) with methanolic sulphuric acid and monitoring of the reaction by t.l.c. did not reveal the formation of the starting osazones (1) and (10). However the racemization at C-3 can be explained by formation of a 2-phenylazo-2-ene intermediate, as suggested [11,25,26] for the hexulose analogues.

The mass spectra of compounds (6)—(9) (Table 3), showed molecular ion peaks ($M + 1$ and $M$) at $m/z$ 278 and 277, respectively. The base peak occurred at $m/z$ 174 for both the furanosyl *C*-nucleosides (6) and (7) and the pyranosyl analogues (8) and (9). This fragment is characteristic of *C*-nucleosides and is an indication of the *C*-linked furanosyl or pyranosyl group. The peaks corresponding to $BH_2$, BH, and B (= base) (characteristic of *N*-nucleosides) were very weak. The two types of *C*-nucleoside showed the same type of fragmentation with a difference in the intensity of some peaks. The furanosyl analogues (6) and (7) showed greater intensity of the peaks at $m/z$ 200 ($M$ − Ph), 188 ($BHCH_2CHO$), 187 ($BCH_2CHO$), and 73. On the other hand, the pyranosyl analogues (8) and (9) showed a greater abundance at $m/z$ 173 (BCHO), 91 (PhN), and 60.

## EXPERIMENTAL

Evaporations were performed under diminished pressure below 60 °C. T.l.c. was conducted on silica gel (Kieselgel G, Merck) with solvent A (3 : 1 benzene–ethanol), B (2 : 1 : 1 benzene–chloroform–ethanol), or C (4 : 1 : 1 benzene–light petroleum–ethanol). Optical rotations and o.r.d. measurements were obtained at 20 ± 2 °C with a Perkin-Elmer 141 Polarimeter (10 cm, 1 ml microcell). I.r. absorption spectra were recorded with a Perkin-Elmer 337 instrument. U.v. spectra were recorded with a Cary 17 or a Beckman 125 spectrophotometer. N.m.r. spectra were recorded with NTC (360 or 470 MHz) instruments, using internal tetramethylsilane as standard. Mass spectra were recorded with a Finnigan 6100 Data System Gass-Chromatograph/EI-CI spectrometer. High resolution mass spectra were recorded with a CBC 110 double-focusing mass spectrometer.

3,6-*Anhydro*-D-manno-*hept*-2-*ulose Phenylosazone* (2).—D-*gluco*-Hept-2-ulose phenylosazone (1) (10 g) was boiled under reflux with methanolic sulphuric acid (1 200 ml methanol, 0.6 ml conc. sulphuric acid, and 2.4 ml water), for 4 h and the mixture was monitored by t.l.c. After 4 h reflux, t.l.c. revealed the absence of the starting osazone and formation of three more mobile products, $R_F$ 0.56, 0.46, and 0.36 (solvent A), and 0.57, 0.41, and 0.33 (solvent B). The solution was poured into hot water and the methanol was evaporated off under diminished pressure. The precipitate obtained was filtered off, washed with water, and dried; yield 8 g. The mixture (1 g) was purified by chromatography on a column (2 × 50 cm) of silica gel, with solvent A as eluant. The yellow fractions were collected and evaporated to dryness, and *compound* (2) was separated by rechromatography on a column of silica gel, or by preparative t.l.c. It gave yellow crystals m.p. 172—175° (from aqueous methanol), $R_F$ 0.56 (solvent A) and 0.57 (solvent B); $[\alpha]_D^{22}$

+110° (*c* 0.25 in acetone); for n.m.r. data see Table 2 (Found: C, 61.7; H, 6.1; N, 15.0%; $M^+$, 370.165. $C_{19}H_{22}N_4O_4$ requires C, 61.6; H, 6.0; N, 15.15%; *M*, 370.164).

3,6-*Anhydro*-D-gluco-*hept*-2-*ulose Phenylosazone* (3).—This *compound* was isolated from the foregoing mixture by fractional crystallization from aqueous methanol, of the metaial, $R_F$ 0.46 (solvent A) and 0.41 (solvent B); m.p. 165—167°; for n.m.r. data see Table 2 (Found: $M^+$, 370.164).

3,7-*Anhydro*-D-gluco-*hept*-2-*ulose Phenylosazone* (5).—This *compound* was isolated from the mixture by preparative t.l.c. [$R_F$ 0.36 (solvent A), 0.33 (solvent B)] as yellow crystals, m.p. 187—188° (from aqueous methanol); $[\alpha]_D^{22}$ −27.8 (*c* 1.01 in acetone); for n.m.r. data see Table 2 (Found: C, 61.7; H, 6.1; N, 15.0%; $M^+$, 370.167).

Treatment of D-*manno*-hept-2-ulose phenylosazone (10) (12 g) with methanolic sulphuric acid (1 500 ml) for 4 h, and processing as described for (1), gave an anhydro-osazone mixture containing three components having the same mobility on t.l.c. (solvents A, B, and C) as the mixture obtained from (1).

*Conversion of the Anhydro-osazone Mixture from* D-gluco-*Hept*-2-*ulose Phenylosazone into* 2-*Phenyltriazole* C-*Nucleoside Analogues*.—A suspension of the crude anhydro-osazone mixture (30 g) obtained from (1) in water (200 ml) was boiled under reflux with stirring, and copper sulphate (30 g) in water (200 ml) was added dropwise, followed by propan-1-ol (2 ml). The mixture was refluxed for 10 h, treated with charcoal, and filtered. The filtrate was evaporated to dryness, and the residue was extracted with boiling butan-2-one (3 × 300 ml). The extracts were combined and filtered from inorganic materials, and the filtrate was evaporated to a syrup. T.l.c. showed three main spots, $R_F$ 0.50, 0.46, 0.42 (solvent A), 0.78, 0.74, 0.64 (solvent B), and 0.34, 0.31, 0.24 (solvent C). The mixture was dissolved in dilute methanol, applied to a column (4 × 75 cm) of Dowex 1-X8 ($OH^-$) ion-exchange resin and eluted with 30%, 60%, and 90% aqueous methanol.

4-α-D-*Arabinofuranosyl*-2-*phenyl*-v-*triazole* (6).—The 90% methanol fractions upon evaporation and crystallization from methanol–benzene (or water) gave colourless *needles* m.p. 160°; yield 3.1 g; $R_F$ 0.50 (A), 0.78 (B), and 0.34 (C); $[\alpha]_D^{22}$ +83.1° (*c* 1.2 in methanol; $\nu_{max.}$ (KBr) 3 380 (OH), 1 600 (C=N), 1 500, and 760 $cm^{-1}$ (Ph); $\lambda_{max.}$ (MeOH) 266 nm (1 og ε 4.3); o.r.d. in methanol: $[\phi]_{589}$ +238°, $[\phi]_{578}$ +241°, $[\phi]_{546}$ +279°; for n.m.r. and mass spectral data see Tables 1 and 3; periodate consumption 1.04 mol equiv. (based on *M* 377) [in a control experiment using methyl α-D-mannopyranoside under the same conditions for all compounds 2.04 mol equiv. of periodate were consumed (based on *M* 194)] (Found: C, 56.55; H, 5.6; N, 14.9%. $C_{13}H_{15}N_3O_4$ requires C, 56.3; H, 5.45; N, 15.15%; *M*, 277.106).

A pure sample of (2) on refluxing with copper sulphate and processing as described before gave compound (6), m.p. and mixed m.p. 158—160°.

4-β-D-*Arabinofuranosyl*-2-*phenyl*-v-*triazole* (7).—This *compound* was eluted from the ion-exchange column with 60% methanol; it was crystallized from butan-2-one–hexane; yield 4.8 g; m.p. 80—81°; $R_F$ (0.46 (A), 0.74 (B), 0.29 (C); $[\alpha]_D^{22}$ +22.7° (*c* 0.96 in methanol); $\nu_{max.}$ (KBr) 3 360 (OH), 1 550 (C=N), 1 460, and 750 $cm^{-1}$ (Ph); $\lambda_{max.}$ (MeOH) 267 (log ε 4.3); o.r.d. in methanol: $[\phi]_{589}$ +66°, $[\phi]_{578}$ + 68°, $[\phi]_{546}$ +76°, $[\phi]_{436}$ +105°, $[\phi]_{365}$ +103°; for n.m.r. and mass spectral data see Tables 1 and 3; periodate consumption 1.2 mol equiv. (Found: C, 56.05; H, 5.35; N, 15.0. $C_{13}H_{15}N_3O_4$ requires C, 56.3; H, 5.45; N, 15.15%).

4-α-D-*Arabinopyranosyl*-2-*phenyl*-v-*triazole* (8).—This was eluted from the column with 30% methanol [after elution of compound (9)] and crystallized from methanol–benzene as colourless *needles*; m.p. 142—144°; yield 0.3 g; $R_F$ 0.45 (A), 0.72 (B), 0.31 (C); $[\alpha]_D^{22}$ +66.2° (*c* 0.13 in methanol), $\nu_{max.}$ (KBr) 3 350 (OH), 1 550 (C=N), 1 490, and 760 $cm^{-1}$ (Ph); $\lambda_{max.}$ (MeOH) 266 (log ε 3.7); o.r.d. in methanol; $[\phi]_{589}$ +183°, $[\phi]_{578}$ +196°, $[\phi]_{436}$ +426°, and $[\phi]_{365}$ +795°; for n.m.r. and mass spectra see Tables 1 and 3; periodate consumption 2.08 mol equiv. (Found: C, 56.55; H, 5.55; N, 15.1%; $M^+$, 277.107).

TABLE 1

Chemical shifts (δ) and first-order coupling constants (*J* Hz) for compounds (6)—9) at 470 MHz in $(CD_3)_2SO$

| | Glycosyl ring | | | | | | | 2-Phenyltriazole | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | H-1′ | H-2′ | H-3′ | H-4′ | H-5′ | | OH | H-5 | *o*- | *m*- | *p*- |
| (6) | 5.22d<br>$J_{1',2'}$ 3.6 | 4.02—4.05m | | 3.84m | 3.61—3.69m | | 5.38d<br>*J* 3.6<br>5.20d<br>*J* 6.0<br>5.03m | 7.99s | 8.01d | 7.56t | 7.41t |
| (7) | 4.87d<br>$J_{1',2'}$ 6.3 | 4.19t<br>$J_{2',3'}$ 5.8 | 3.97t<br>$J_{3',4'}$ 4.8 | 8.88m | 3.59dd<br>$J_{4',5'}$ 5.3 | 3.51dd<br>$J_{4',5'}$ 5.3<br>$J_{5',5'}$ 12 | 5.51d<br>*J* 5.7<br>5.29d<br>*J* 4.8<br>4.83<br>*J* 5.7 | 8.09s | 8.00d | 7.57t | 7.42t |
| (8) | 4.92s | 3.75d<br>$J_{1',2'}$ 2.7 | 3.84m<br>$J_{3',3'}$ 3 | 3.92m | 3.63dd<br>$J_{4',5'}$ 5.4 | 3.56t<br>$J_{4',5'}$ 0<br>$J_{5',5'}$ 10.5 | 5.05d<br>*J* 5.4<br>5.01s<br>4.62d<br>*J* 6.5 | 7.94s<br>7.94s | 7.98d<br>7.98d | 7.55t<br>7.55t | 7.40t<br>7.40t |
| (9) | 4.26d<br>$J_{1',2'}$ 9.6 | 3.83t<br>$J_{2',3'}$ 2.1 | 3.80t<br>$J_{3',4'}$ 3.4 | 3.78m | 3.64d<br>$J_{4',5'}$ 0<br>$J_{5',5'}$ 12 | 3.47dd<br>$J_{4',5'}$ 3.3<br>$J_{5',5'}$ 9.0 | 4.91d<br>*J* 5.9<br>4.79d<br>*J* 5.6<br>4.61d<br>*J* 3.7 | 8.03s | 8.01d | 7.57t | 7.42t |

TABLE 2

Chemical shifts (δ) and first-order couplings (*J* Hz) for compounds (2), (3), and (5) at 360 MHz, in $(CD_3)_2CO$

| | Glycosyl ring | | | | | | | Bis(phenylhydrazone) | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | H-1′ | H-2′ | H-3′ | H-4′ | H-5′ | | OH | Aromatic protons | CH=N | NH non-chelated | NH chelated |
| (2) | 4.47s $J_{1',2'}$ *ca.* 1 | 4.03—4.12m | | *a* | 3.73m | 3.64m $J_{5',5'}$ 10.4 | 4.44d *J* 4.3<br>4.18d *J* 3.4<br>3.80d *J* 7 | 6.85—7.36m | 7.81s | 10.69s | 12.28s |
| (3) | 4.49d $J_{1',2'}$ 6.8 | 4.37t $J_{2',3'}$ 5.7 | 4.13t $J_{3',4'}$ 5.9 | 3.98m | 3.77dd $J_{4',5'}$ 3.4 | 3.70dd $J_{4',5'}$ 4.9<br>$J_{5',5'}$ 11.9 | 3.96<br>4.53bs<br>4.65bs | 6.86—4.49m | 7.79s | 9.86s | 12.28s |
| (5) | 4.00d $J_{1',2'}$ 9.1 | 3.92d *J* 9.5 | 3.98m | 3.97m $J_{3',4'}$ 4.9 | 3.74dd $J_{4',5'}$ 3.3 | 3.67d $J_{5',5'}$ 11.5 | 4.2d *J* 4.6<br>4.16d *J* 4.4<br>3.85d *J* 5.7 | 6.86—7.38m | 7.78s | 9.86s | 12.28s |

[a] Obscured by H-5′.

4-β-D-*Arabinopyranosyl*-2-*phenyl*-v-*triazole* (9).—This was eluted from the ion-exchange column with 30% methanol; recrystallization from methanol–benzene gave colourless *needles* (0.55 g); m.p. 134—135°; $R_F$ 0.42 (A), 0.64 (B), 0.24 (C); $[\alpha]_D^{22}$ −56.5 (*c* 1.01 in methanol); $\nu_{max.}$ (KBr) 3 335 (OH), 1 590 (C=N), 1 490, and 758 $cm^{-1}$ (Ph); $\lambda_{max.}$ (MeOH) 267 nm (log ε 4.0); o.r.d. in methanol: $[\phi]_{589}$ −157°, $[\phi]_{578}$ −185°, $[\phi]_{436}$ −318°, $[\phi]_{365}$ −518°; for n.m.r. and m.s. data see Tables 1 and 3; periodate consumption 2.15 mol equiv. (Found: C, 56.15; H, 5.4; N, 14.85%; $M^+$, 277.106).

TABLE 3

Relative intensities (%) of predominant ions in the mass spectra of compounds (6)—(9)

| | | % | | | |
|---|---|---|---|---|---|
| *m/z* | Fragment | (6) | (7) | (8) | (9) |
| 278 | *M* + 1 | | | 1 | 1 |
| 277 | *M* | 3 | 4 | 8 | 8 |
| 200 | *M* − Ph | 16 | 11 | 1 | 2 |
| 188 | $BHCH_2CHO$ | 55 | 62 | 3 | 5 |
| 187 | $BCH_2CHO$ | 16 | 23 | 6 | 8 |
| 175 | B + 31 | 22 | 17 | 17 | 17 |
| 174 | BCHOH | 100 | 100 | 100 | 100 |
| 173 | BCHO | 9 | 9 | 40 | 46 |
| 172 | BCO | 8 | 10 | 6 | 6 |
| 159 | $BHCH_2$ | 2 | 4 | 8 | 7 |
| 158 | $BCH_2$ | 22 | 28 | 20 | 18 |
| 146 | $BH_2$ | 2 | | 1 | 2 |
| 145 | BH | | | 0.5 | 0.3 |
| 144 | B (=base) | | | 0.6 | 0.7 |
| 118 | B − CN | | | 4 | 4 |
| 117 | B − HCN | 5 | 5 | 3 | 4 |
| 103 | PhCN | 7 | 4 | 7 | 7 |
| 93 | $PhNH_2$ | 6 | | 6 | 8 |
| 92 | PhNH | 22 | 26 | 27 | 28 |
| 91 | PhN | 49 | 65 | 74 | 78 |
| 78 | PhH | 6 | 6 | 11 | 9 |
| 77 | Ph | 60 | 52 | 60 | 62 |
| 73 | | 39 | 50 | 14 | 16 |
| 60 | | 39 | 50 | 83 | 89 |

*Conversion of the Anhydro-osazone Mixture from* D-manno-*Hept-2-ulose Phenylosazone into the* C-*Nucleoside Analogue Mixture*.—The crude D-*manno*-hept-2-ulose anhydro-osazones (3 g) in methanol (100 ml) were boiled under reflux and treated with a solution of copper sulphate (3 g) in water (100 ml). Then propan-1-ol (2 ml) was added, and the refluxing was continued for 6 h. The mixture was filtered and the filtrate stirred with Amberlite IR MB ion exchange resin, which was filtered off and washed thoroughly with methanol. Filtrate and washings were combined and evaporated to a syrup, which was separated on a column of Dowex 1-X8 ($OH^-$) ion-exchange resin. Elution with 30% methanol (1 l), evaporation to dryness, and crystallization from methanol–benzene gave compound (9) as colourless needles; m.p. and mixed m.p. 132—134°. The 60% methanol eluate gave compound (8) as a colourless needles, m.p. and mixed m.p. 140—142°, and the 90% methanol eluate gave compound (7) m.p. and mixed m.p. 80—82°, and compound (6) m.p. and mixed m.p. 158—160°.

The author thanks the Purdue University Biochemical Magnetic Resonance Laboratory for the 360 and 470 MHz n.m.r. spectral measurements, which were supported by N.I.H. Thanks are due to Dr. J. L. Markley for making available these facilities, and Mr. D. H. Croll and Mr. T. M. Chan for recording the spectra. Thanks are also due to Dr. F. E. Regnier and Mr. M. Goodwin for mass spectral measurements.

[1/934 *Received*, 11*th June*, 1981]

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