Arylazo-glycenosides. Part 8.[1] Synthesis and Reactions of Some 2- and 3-Arylazo-derivatives of Methyl 4,6-*O*-Benzylidene-2,3-dideoxy-D-*threo*-hex-2-enopyranosides

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Preparations are described of the α- and β-anomers of methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-D-*threo*-hex-2-enopyranoside and of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-α-D-*threo*-hex-2-enopyranoside using D-galactose as the initial material. The procedures adopted for the syntheses are essentially those developed in our laboratory for the preparation of phenylazo-derivatives of sugars, as described in Part 1 of this series of papers.†

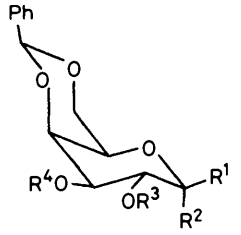
The 1,4-addition reactions of the new phenylazo-derivatives with a range of nucleophiles have been investigated and the results have been compared with those obtained previously with analogous compounds having the D-*erythro* configuration. The adducts from the benzylidenated phenylazo-glycenosides in which the acetal and pyranoid rings are *cis*-fused are found to be relatively unstable in solution and readily revert to the parent phenylazo-glycenoside.

From methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-α-D-*threo*-hex-2-enopyranoside, isolable adducts were obtained in reactions with methylamine, dimethylamine, benzylamine, or hydride ion. Also, stable products were formed in the 1,4-addition reactions of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-α-D-*threo*-hex-2-enopyranoside with benzylamine, benzenethiol, dimethylamine, or ammonia (followed by acetylation of the ammonia adduct).

In continuation of our studies of arylazo-glycenosides,[2-7] and particularly our investigation of the value of such compounds as intermediates in syntheses of modified sugars, we have prepared methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-α- and β-D-*threo*-hex-2-enopyranoside and methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-phenylazo-α-D-*threo*-hex-2-enopyranoside from D-galactose by the sequence of reactions described in earlier papers in this series.[2,4,5,7] Nucleophilic addition reactions of these compounds have been compared with those for the corresponding compounds having the D-*erythro* configuration. In the former compounds the two six-membered rings are *cis*-fused whereas in the latter the ring fusion is *trans*. It has been found that arylazo-glycenosides with a *cis*-fused *O*-benzylidene ring undergo addition–elimination reactions more readily than do the analogous compounds with a *trans*-fused acetal ring.

Methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (1) and its β-anomer (2) were prepared conventionally and were subjected to monobenzoylation. When the glycoside (1) was treated at 0 °C with benzoyl chloride (1 equiv.) in pyridine, reaction was slow and was incomplete even after 24 h. The products were separated by chromatography to yield the 3-benzoate (3) as the major product (30%) with a smaller amount of the 2-benzoate (4) (20%) and some 2,3-dibenzoate (5) (15%).[8] Addition of more benzoyl chloride and a longer reaction time led to an increase in the amount of the 2,3-dibenzoate (5). Several other benzoylating agents and reaction conditions were tested, including 1-benzoylimidazole in chloroform (a reagent which can show high selectivity)[9,10] which gave compounds (3), (4), and (5) in 15, 12.5, and 30% yield, respectively; the use of a phase-transfer catalyst as described by Lynda *et al.*[11] [compounds (3) : (4) : (5) = 15 : 40 : 15%]; and benzoyl cyanide–triethylamine [12] [compounds (3) : (4) : (5) = 41 : 21 : 18.5%].

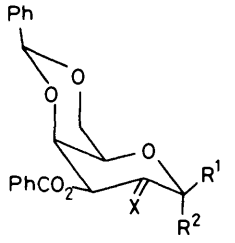
When methyl 4,6-*O*-benzylidene-β-D-galactoside (2) was benzoylated with benzoyl cyanide–triethylamine in acetonitrile the 3-ester (6) was obtained in 69% yield with only 5% of the 2-ester (7) and 10% of the 2,3-diester (8). Russian workers [13] have reported that benzoylation of the glycoside (2) with benzoyl chloride and 1-benzoylimidazole in chloroform gave the 3-ester (6) (58%) from which the 2-ester (7) impurity could be separated by column chromatography over silica. Compound (6) can be isomerised to the ester (7) by treatment with sodium hydroxide. There were differences between the physical constants of our compounds and those reported by Veinberg *et al.*[13] but the ^{1}H n.m.r. spectra of the monobenzoates (3), (4), (6), and (7) were in accord with the assigned structures, as were the ^{1}H n.m.r. spectra of the ulosides derived from the monobenzoates.

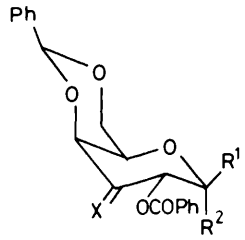


(1) $R^1 = R^3 = R^4 = H$, $R^2 = OMe$
(2) $R^1 = OMe$, $R^2 = R^3 = R^4 = H$
(3) $R^1 = R^3 = H$, $R^2 = OMe$, $R^4 = COPh$
(4) $R^1 = R^4 = H$, $R^2 = OMe$, $R^3 = COPh$
(5) $R^1 = H$, $R^2 = OMe$, $R^3 = R^4 = COPh$
(6) $R^1 = OMe$, $R^2 = R^3 = H$, $R^4 = COPh$
(7) $R^1 = OMe$, $R^2 = R^4 = H$, $R^3 = COPh$
(8) $R^1 = OMe$, $R^2 = H$, $R^3 = R^4 = COPh$

The monobenzoates (3), (4), and (6) were oxidised with systems based on dimethyl sulphoxide (DMSO) [*i.e.* DMSO–DCC (dicyclohexylcarbodi-imide)–H_3PO_4; DMSO–Ac_2O; DMSO–P_4O_{10}] but the best yields of the hexosiduloses (9), (10), and (11), respectively, were obtained with DMSO–DCC–H_3PO_4 as oxidant,[14] as described by Baker and Buss.[15] The structures of the ulosides (9), (10), and (11) were deduced

† See reference 2.





(9) R^1 = H, R^2 = OMe, X = O

(10) R^1 = H, R^2 = OMe, X = O

(11) R^1 = OMe, R^2 = H, X = O

(12) R^1 = H, R^2 = OMe, X = NNHPh

(13) R^1 = H, R^2 = OMe, X = $NNHC_6H_4NO_2$-4

(14) R^1 = H, R^2 = OMe, X = $NNHC_6H_3(NO_2)_2$-2,4

(15) R^1 = OMe, R^2 = H, X = $NNHC_6H_4NO_2$-4

(16) R^1 = OMe, R^2 = H, X = $NNHC_6H_3(NO_2)_2$-2,4

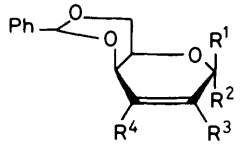
(17) R^1 = H, R^2 = OMe, X = $NNHC_6H_3(NO_2)_2$-2,4

from their ^{1}H n.m.r. spectra. The signal for the anomeric proton in methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*lyxo*-hexopyranosidulose (9) appeared as a singlet at δ 4.91. For compound (11) the anomeric proton gives a signal at δ 5.06: expansion of the spectrum showed 1-H—3-H coupling ($J_{1,3}$ 0.7 Hz). Thus, the signal of the (axial) anomeric proton in compound (11) resonates at 0.15 p.p.m. lower field than that of the α-D-anomer (9) (*cf.* reference 2). These results can be rationalised in terms of the anisotropy of the carbonyl group.[16,17] The anomeric proton in compound (10) gave a signal at δ 5.5 with $J_{1,2}$ 7 Hz (eq–ax coupling).

The arylhydrazones (12)—(17) were prepared by treatment of the appropriate hexosidulose with the corresponding arylhydrazine in dimethylformamide (DMF) and glacial acetic acid.[18] The use of DMF had the advantages over other solvents of giving purer products and higher yields. Although the crystalline phenylhydrazone (12) can be stored indefinitely, other phenylhydrazones were not obtained and when the uloside (10) or (11) was treated with phenylhydrazine the products were, respectively, the phenylazo-alkenes (18) and (20). A convenient method for conversion of an arylhydrazone containing an α-leaving group into an azo-alkene is treatment with a base (methoxide,[2] t-butoxide,[2] and 1,5-diazabicyclo-[5.4.0]undec-5-ene [5] have been used successfully). For the preparation of the phenylazo-derivative (19) from the phenylhydrazone (12), t-butoxide was used.

Monitoring by t.l.c. indicated that the appropriate arylazo-glycenoside is formed when the uloside (9), (10), or (11) is treated with phenylhydrazine or 4-nitrophenylhydrazine in the absence of glacial acetic acid. No isolable products were obtained under these conditions when the ulosides were treated with 2,4-dinitrophenylhydrazine, and attempts to convert the dinitrophenylhydrazones (14), (16), and (17) into the corresponding azo-alkenes by using prolonged reaction times were unsuccessful.[1,19]

The phenylazo-glycenosides (18), (19), and (20) exhibited ultraviolet absorption in the region 302—305 nm, a shift of 20—25 nm to longer wavelength from the absorption maximum shown by the uloside phenylhydrazone (12) ($\lambda_{max.}$ 278 nm). These values are comparable to others reported previously [2,5] and the value for the phenylhydrazone (12) is close to that observed for phenylhydrazone derivatives of similar ketones [20,21] and similar to that reported generally for phenylhydrazones of ketones.[22,23] All the arylhydrazones (12)—(17) exhibited very strong i.r. absorptions at *ca.* 1 600 cm^{-1} due to the C=NNHAr group [22,24,25] and, in addition showed a diagnostic sharp absorption close to 3 300 cm^{-1} due to the N–H group.



(18) R^1 = R^3 = H, R^2 = OMe, R^4 = N=NPh

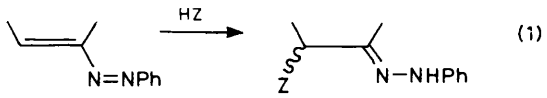
(19) R^1 = R^4 = H, R^2 = OMe, R^3 = N=NPh

(20) R^1 = OMe, R^2 = R^4 = H, R^3 = N=NPh

It is known that arylhydrazones of glycopyranosiduloses can exist as geometric isomerides.[2,5,26] The arylhydrazones now reported were each obtained in one geometric form. On the basis of the method adopted by Karabatsos and his co-workers,[27] the 4-nitrophenylhydrazone (13) was assigned the *syn**-structure because the 1-H signal suffered an upfield shift (+0.34 p.p.m.) and 3-H suffered a downfield shift (−0.02 p.p.m.) in [$^2H_6$]benzene relative to their chemical shifts in $CDCl_3$, and hence the $O_2NC_6H_4NH$ group was nearer to 1-H than to 3-H.

The structures of the phenylazo-alkenes (18)—(20) follow from their method of formation, their elemental analysis, their orange-yellow colour, and their characteristically intense u.v. absorption at 302—305 nm. Mass-spectral measurements and n.m.r. spectra support the structural assignments. In the mass spectra of the phenylazo-glycenosides (18) and (19) a molecular-ion peak (M^+) appeared at 352. For compound (18) there were abundant peaks at *m/z* 77, 91, and 105 (*cf.* reference 2) due to $C_6H_5^+$, $C_7H_7^+$, and $C_6H_5N_2^+$ ions, respectively.[28] The first of these is the base peak and presumably is made up of contributions from both phenyl groups present in the molecule. For the azo-alkene (19) the base peak is at *m/z* 187 and there are strong peaks at *m/z* 91, 121, 149, and 203. The latter two peaks arise from the h_2-ion [$PhCH=\overset{+}{O}CH_2CHO$] and h_1-ion [$O=CH-CH=C(N_2Ph)\cdot CH=\overset{+}{O}CH_3$] formed by the 'h-fragmentation' pathway that benzylidene derivatives have been shown [29] to undergo. The ^{1}H n.m.r. spectrum of each compound (18), (19), and (20) shows the presence of only two phenyl groups, one vinylic proton, but no NH signal (a feature

* In this paper the *syn*-form is regarded as the isomer in which the arylamino-group is directed towards the ring-carbon atom with lowest number: the other isomer is the *anti*-form (see reference 26 and also P. M. Collins, *Chem. Commun.*, 1966, 164).



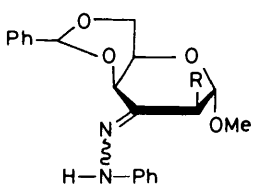
(1)

confirmed by the i.r. spectra). All these observations are consistent with the structures proposed for the phenylazo-glycenosides, each being formed by an eliminative loss of benzoic acid from an intermediate benzoylated phenylhydrazone.

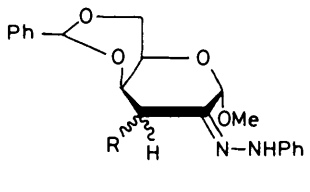
Addition Reactions to Azo-alkenes.—Following the findings reported previously [2] on the addition reactions undergone by arylazo-glycenopyranosides, such reactions were attempted with the arylazo-glycenosides (18)—(20). The onset of addition could be observed from the colour change (deep-orange to light-yellow) of the reaction mixture. 1,4-Addition across the azo-alkene system leads to formation of an α-substituted phenylhydrazone, reaction (1). Thus, addition to compound (18) would lead to a 2-substituted 3-phenylhydrazone derivative of a hexopyranosidulose whereas compounds (19) and (20) should afford 3-substituted 2-phenylhydrazone derivatives. To examine the stereochemistry of the adducts, ^{1}H n.m.r. spectral measurements were carried out and recourse was made to the correlation [30] that exists between vicinal coupling constants and stereochemistry in six-membered cyclic systems. This is a method adopted previously to study the adducts from analogous arylazo-glycenosides with the D-*erythro* configuration.[2] The generalisation usually made [31] is that $J_{ax,ax} > 8$ Hz and $J_{ax,eq}$ and $J_{eq,eq} < 6$ Hz. This has been further refined by Coxon [32] who found that the values for $J_{1,2}$ for several methyl α-D-glycopyranosides were 4 Hz > $J_{eq,ax}$ > 2 Hz > $J_{eq,eq}$. This empiricism is supported by observations made with several β-glycopyranosides.[33-35] Hence, it is usually a simple matter to verify an axial–axial relationship between two vicinal protons but to decide between an axial–equatorial and an equatorial–equatorial relationship is more difficult, particularly as the electronegativity of the substituents attached to the carbon atoms bearing the coupled hydrogen atoms can affect the degree of coupling. However, the method has been used successfully in analyses comparable to those now described.

Initial attempts to form adducts were discouraging and with some nucleophiles the reactions of compounds (18), (19), or (20) were inconclusive: either decomposition occurred or, when evidence of addition *was* achieved, the adduct was unstable and on attempted isolation it reverted to starting materials. For example, although the colour change and t.l.c. monitoring indicated that the phenylazo-glycenoside (18) undergoes reaction with sodium azide in acetone, or sodium methoxide in methanol, or sodium borohydride in methanol [t.l.c., solvents *b*, *c*, and *e*, respectively (solvents defined in Experimental section, *Methods*)] the crude products obtained (which showed absorption for a hydrazone function) underwent decomposition on attempted purification in organic solvents.

No adducts were obtained when compound (20) was treated under moderate conditions with azide, methoxide, benzenethiolate or amines in solvents such as methanol, ethanol, or DMF. Although the azo-alkene (19) undergoes reaction with sodium methoxide in methanol at room temperature, as shown by a colour change in the reaction mixture and t.l.c. monitoring, attempts to isolate the product led to breakdown of the adduct and reformation of compound (19). Clearly, addition–elimination occurs more readily in this series of compounds with the D-*threo* configuration than with those of the D-*erythro* configuration.[2] In this connexion it is of



(21) R = $NHCH_2Ph$
(22) R = SPh
(23) R = NMe_2
(24) R = NHCOMe



(25) R = NHMe
(26) R = NMe_2
(27) R = $NHCH_2Ph$
(28) R = H

Compounds (25)—(27) are each 1 epimer of unspecified stereochemistry at C(3), NOT an epimeric mixture

interest to note the results of Baer and his co-workers [36] who have studied extensively the addition reactions of methyl 4,6-*O*-benzylidene-2,3-dideoxy-3-nitro-β-D-*erythro*-hex-2-enopyranoside and its C(4)-epimer (derived from 3-nitrogalactopyranoside). For the D-*erythro*-isomer most of the addition reactions, particularly when carried out under basic conditions, proceed with a high degree of selectivity to give mainly products with the substituents at C(2) and C(3) *trans*-located with the D-*gluco* configuration. A similar result was reported for the α-D-anomer of the 3-nitro-enopyranoside.[37] However, for the C(4)-epimer with the D-*threo* configuration, attempted addition of ammonia across the double bond resulted in the loss of the benzylidene group, presumably by a β-elimination process, giving rise to a mixture of products. Under less basic conditions an addition product was obtained but in poor yield.[38] The type of ring fusion has an influence on the course of the addition reaction. Other examples of easy addition–elimination reactions have been observed in our laboratory.[39]

In spite of these discouraging results, some adducts were isolated successfully. It was found that the reaction of benzylamine with compound (18) was rapid at room temperature and it was possible to isolate the adduct in crystalline form. It showed the anticipated i.r., u.v., and ^{1}H n.m.r. spectral characteristics for a 2-benzylamino-3-phenylhydrazone of a methyl hexopyranosidulose. The coupling constant ($J_{2,1}$ 2 Hz) is consistent with the protons at C(2) and C(1) being disposed equatorial–equatorial thereby locating the benzylamino-group at C(2) in an axial position. On this basis the compound apparently is methyl 2-benzylamino-4,6-*O*-benzylidene-2-deoxy-α-D-*lyxo*-hexopyranosid-3-ulose phenylhydrazone (21).

Likewise, crystalline adducts were obtained when the azo-alkene (18) was treated with either benzenethiolate, dimethylamine, or ammonia followed by acetylation. In each case reaction was rapid. Respectively, the products are considered to have the structures (22), (23), and (24), but the configuration at C(2) is not proven unequivocally. Each compound showed i.r. and u.v. spectra consistent with the phenylhydrazone structure. A signal at δ 8.07 in the 250 MHz ^{1}H n.m.r. spectrum of compound (22) confirmed the presence of an amino-proton: other salient features were doublets at δ 5.08 (assigned to the anomeric proton) and δ 4.99 (assigned to 2-H). The value of $J_{2,1}$ was 2.2 Hz. As C(1)–H is equatorial in this compound in its most likely conformation, this coupling indicates that C(2)–H is also equatorially disposed which indicates a D-*lyxo* configuration for the compound. The configurations shown in the formulae for compounds (23) and (24) are based on analogy. For the 2-dimethylamino-compound (23) this could not be tested because the adduct underwent elimination when its solution in $CDCl_3$ was being used for ^{1}H n.m.r. spectra determinations and so interpretable spectra could not be obtained. In the 250 MHz ^{1}H n.m.r. spec-

trum of compound (24) a signal at δ 9.08 was assigned to the NH proton (exchangeable with D_2O) of the phenylhydrazone. Signals at δ 4.89 and 5.03 were assigned to 1-H and 2-H, respectively. There was a large coupling (10 Hz) between 2-H and the N–H proton of the geminal acetamido-group. The deshielding influence of the acetamido-group at C(2) resulted in the proton at C(2) being at low field relative to that at C(1).

From the phenylazo-glycenoside (19) crystalline adducts were obtained with methylamine, dimethylamine, benzylamine, or sodium borohydride. The elemental analysis and spectral characteristics of each adduct were consistent with the products being 3-substituted derivatives of methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*lyxo*-(or *xylo*-) hexopyranosidulose phenylhydrazone, *i.e.* compounds (25)—(28). Analysis of the ^{1}H n.m.r. spectrum of the methylamine adduct (25) revealed a signal at δ 3.6 (d, 3-H) with $J_{3,4}$ 3.5 Hz. The proton at C(4) gave a signal at δ 4.26 (dd) with $J_{4,3}$ 3.5 and $J_{4,5}$ 2 Hz. If 4-H is equatorial this would point to 3-H being axial and to compound (25) having the D-*lyxo* configuration. The spectra of compounds (26) and (27) were not interpretable owing to solutions of the substances in $CDCl_3$ undergoing decomposition during the spectral measurements.

When compound (19) was reduced with sodium borohydride in methanol it afforded a single product which analytical and spectral evidence indicated was methyl 4,6-*O*-benzylidene-3-deoxy-α-D-*threo*-hexopyranosidulose phenylhydrazone (28). In an attempt to ascertain the stereochemistry of the hydride addition, the reaction was repeated under identical conditions with sodium borodeuteride in methan[^{2}H]ol. With methyl 4,6-*O*-benzylidene-2,3-dideoxy-2-phenylazo-α-D-*erythro*-hex-2-enopyranoside a change from borohydride to borodeuteride had led to products from which useful information could be deduced.[2] Each reagent led to a 3-deoxyglycopyranosidulose phenylhydrazone but the 3-deuterio-product had shown a simplification of the C(3)-methylene signals observed in the ^{1}H n.m.r. spectrum when compared with the non-deuteriated product. This enabled the configuration to be deduced as D-*ribo* and thereby led to information about the stereochemistry of the reduction. Unfortunately, the second-order ^{1}H n.m.r. spectrum of the deuteride reduction of compound (19) was less informative, particularly as regards the multiplicity of the C(3)-methylene signals, and it seems possible that hydride addition may have taken place from both directions.

A comparison of the 2- and 3-phenylazo-derivatives of methyl 4,6-*O*-benzylidene-2,3-dideoxy-D-hex-2-enopyranosides having the D-*erythro* and D-*threo* configurations reveals the greater difficulty of working with the D-*threo* compounds. Whereas relatively stable 1,4-adducts are formed by the phenylazo-derivatives of D-*erythro* configuration in which the acetal and pyranoid rings are *trans*-fused, the adducts from the benzylidenated D-*threo*-phenylazo-glycenosides with a *cis*-fused ring system are relatively unstable and difficult to examine in solution.

Experimental

Methods.—I.r. spectra were measured with a Perkin-Elmer Infracord model 137: solid samples were dispersed in KBr and gums were smeared on KBr discs; u.v. spectra were obtained for 96% ethanolic solutions with a Perkin-Elmer spectrophotometer model 402; optical rotations were measured on solutions in chloroform (unless otherwise stated) with a Bellingham and Stanley polarimeter; mass spectra were measured with an A.E.I. MS 902 instrument operated with an ionising potential of 70 eV and a probe inlet temperature of 150 °C; n.m.r. spectra were determined with either a JEOL M 100 instrument, a Varian H.A. 220 spectrometer, a Bruker W.M. 250 instrument, or a JEOL FX 200 F.T. spectrometer: ^{1}H spectra were measured at 100 MHz unless otherwise stated and measurements were carried out on solutions in $CDCl_3$ (with internal Me_4Si) unless indicated otherwise: the *J* values cited in this paper are line spacings which were deduced by first-order analysis of the n.m.r. spectra. T.l.c. (thin-layer chromatography) was carried out on Kieselgel GF_{254} (Stahl) with one of the following solvent systems (v/v): (*a*) benzene; (*b*) benzene–ethyl acetate (5 : 1); (*c*) benzene–ethyl acetate (8 : 1); (*d*) benzene–methanol (20 : 1); (*e*) chloroform–diethyl ether (4 : 1); (*f*) methylene dichloride; (*g*) methylene dichloride–ethyl acetate (4 : 1); (*h*) methylene dichloride–ethyl acetate (9 : 1): compounds were located with *p*-anisaldehyde–sulphuric acid or with a u.v. lamp: purity of samples was tested by t.l.c. analysis in two different solvent systems; p.l.c. (preparative layer chromatography) was effected on glass plates (100 × 20 cm) coated to a depth of 0.1 mm with Kieselgel GF_{254} (Stahl): the compound in a volatile solvent was applied by means of a Buckard t.l.c. applicator (type S.A 100); the plate was developed by vertical ascent of the solvent and components were located with a u.v. lamp. Fractions were retrieved by washing them from the silica gel with either acetone or ethyl acetate; column chromatography was carried out on Kieselgel columns which had been wet-packed. Light petroleum refers to that fraction boiling in the range 40—60 °C.

Preparation of Methyl Glycopyranosiduloses.—Methyl 2-*O*-*benzoyl- and* 3-O-*benzoyl*-4,6-O-*benzylidene*-α-D-*galactopyranoside* (4) *and* (3). (*a*) A solution of benzoyl chloride (14 ml) in pyridine (25 ml) was added during 1 h to a cooled (0—5 °C), stirred solution of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (1) [40] (28 g) in pyridine (60 ml). After a further 4 h the reaction mixture was warmed to room temperature and was so maintained overnight. Ice–water (750 ml) was then added to the vigorously stirred mixture and the solid which separated was collected by filtration and was washed with cold water (2 × 150 ml). A solution of the solid in chloroform (250 ml) was washed sequentially with 2N hydrochloric acid (100 ml) and with water (3 × 250 ml) and was dried ($MgSO_4$). Evaporation of the solvent gave a syrupy residue of mixed benzoates which was separated on a column of silica gel (solvent *h*). The fractions were monitored by t.l.c. Methyl 2,3-di-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (5) (7.5 g, 15%) was eluted first. It was obtained as needles, m.p. 201—202 °C; $[\alpha]_D$ +231° (*c*, 0.18); $\nu_{max.}$ 1 710 cm^{-1} (CO) (lit.,[8] m.p. 201—203 °C; $[\alpha]_D^{19}$ +231.3°).

Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (4) (7.6 g, 20%) was obtained as needles from the next set of fractions. It had m.p. 189—190 °C; $[\alpha]_D$ +164.5° (*c*, 0.15); $\nu_{max.}$ 3 600 (OH) and 1 700 cm^{-1} (CO); δ_H 8.24—7.26 (total 10 H, complex m, 2 × Ph), 5.6 (1 H, s, PhC*H*), 5.4 (1 H, dd, $J_{2,3}$ 9, $J_{2,1}$ 4 Hz, 2-H), 5.14 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.46—4.0 (total 4 H, complex m, 3-, 4-, 6-, and 6′-H), 3.78 (1 H, complex m, 5-H), 3.44 (3 H, s, OMe), and 2.48 (1 H, d, OH) (Found: C, 65.1; H, 5.7. Calc. for $C_{21}H_{22}O_7$: C, 65.25; H, 5.75%) (lit.,[8] m.p. 202—204 °C; $[\alpha]_D^{18}$ +145.8 ± 1.7°).

Finally, methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (3) (11.5 g, 30%) was obtained. After recrystallisation from ethanol it had m.p. 139 °C; $[\alpha]_D$ +235.7° (*c*, 1.12); $\nu_{max.}$ 3 500 (OH) and 1 725 cm^{-1} (CO); δ_H 8.24–7.28 (total 10 H, complex m, 2 × Ph), 5.54 (1 H, s, PhC*H*), 5.4 (1 H, dd, $J_{3,2}$ 10, $J_{3,4}$ 4 Hz, 3-H), 5.0 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 4.58—3.98 (total 4H, complex m, 2-, 4-, 6-, and 6′-H), 3.78 (1 H, complex m, 5-H), 3.46 (3 H, s, OMe), and 2.2 (1 H, d, OH) (Found: C, 65.2; H, 5.9. Calc. for $C_{21}H_{22}O_7$: C, 65.25; H, 5.75%) (lit.,[8] m.p. 137—139 °C; $[\alpha]_D^{19}$ +235.7 ± 2°).

(*b*) Triethylamine (0.5 ml) was added to a stirred mixture

of methyl 4,6-*O*-benzylidene-α-D-galactopyranoside (1) (10 g) and benzoyl cyanide (4.7 g) in acetonitrile (50 ml). The reaction was shown to be complete in 15 min (t.l.c., solvent *h*). The light-yellow solution was diluted with methanol (100 ml) and the mixture was stirred for a further 30 min and was then concentrated to afford a syrup. Methanol (2 × 75 ml) was added to and evaporated over the syrup which was then separated chromatographically on a silica-gel column (solvent *h*) to afford the 2-benzoate (4) (2.8 g, 21%), the 3-benzoate (3) (5.5 g, 40%), and the 2,3-dibenzoate (5) (3.2 g, 18.5%), all three identical with authentic samples previously prepared.

Methyl 2-O-*benzoyl- and* 3-O-*benzoyl*-4,6-O-*benzylidene*-β-D-*galactopyranoside* (7) *and* (6). Methyl 4,6-*O*-benzylidene-β-D-galactopyranoside (2) [41] (10 g) and benzoyl cyanide (4.7 g) were stirred in acetonitrile (50 ml) and triethylamine (0.5 ml) was added. After 10 min (complete reaction: t.l.c., solvent *g*) the solution was diluted with methanol (75 ml) and was stirred for a further 30 min. The solution was then concentrated under reduced pressure and methanol (2 × 100 ml) was added to and evaporated over the residue. Fractional crystallisation of the residue from methanol yielded the 3-benzoate (6) (9.5 g, 69%), m.p. 165 °C; $[\alpha]_D$ +94.4° (*c*, 1.1); $\nu_{max.}$ 3 590 (OH) and 1 695 cm^{-1} (CO); δ_H 8.28—7.3 (total 10H, complex m, 2 × Ph), 5.54 (1 H, s, PhC*H*), 5.2 (1 H, dd, $J_{3,2}$ 9, $J_{3,4}$ 4 Hz, 3-H), 4.6—4.0 (total 6 H, complex m, 1-, 2-, 4-, 5-, 6-, and 6′-H), 3.6 (3 H, s, OMe), and 2.56 (1 H, d, OH): the 100 MHz n.m.r. spectrum of the substance in [$^2H_6$]DMSO was essentially the same as that reported by Veinberg *et al.*[13] (Found: C, 65.3; H, 5.7. Calc. for $C_{21}H_{22}O_7$: C, 65.25; H, 5.75%) {lit.,[13] m.p. 163—164 °C (from propan-1-ol); $[\alpha]_D^{23}$ +137° (*c*, 1 in pyridine); ν_{OH} 3 560 cm^{-1}}.

When a solution of the 3-benzoate (6) (5 g) in acetone (250 ml) was treated with 0.05N sodium hydroxide (250 ml) a precipitate was formed. The mixture was kept for 15 min at ambient temperature and was then diluted with ice–water (200 ml). The precipitate was collected by filtration, washed (water, 4 × 100 ml) and dried over KOH *in vacuo*. Recrystallisation from ethanol gave methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-β-D-galactopyranoside (7) (2.1 g, 42%), m.p. 232—233 and 236 °C (from propan-2-ol); $[\alpha]_D$ +28.7 (*c*, 0.4) and +24° (*c*, 0.3 in C_5H_5N); $\nu_{max.}$ 3 540 (OH) and 1 705 cm^{-1} (CO); δ_H ([$^2H_6$]DMSO) 8.18—7.34 (total 10 H, complex m, 2 × Ph), 5.7 (1 H, s, PhC*H*), 5.18 (1 H, td, $J_{2,1}$ 8, $J_{2,3}$ 8 Hz, 2-H), 4.6 (1 H, d, $J_{1,2}$ 8 Hz, 1-H), 4.36—3.44 (total 5 H, complex m, 3-, 4-, 5-, 6-, and 6′-H), and 3.4 (3 H, s, OMe) (Found: C, 65.2; H, 5.75. Calc. for $C_{21}H_{22}O_7$: C, 65.25; H, 5.75%) {lit.,[13] m.p. 250—251 °C (from n-propanol); $[\alpha]_D^{23}$ +43.5° (*c*, 1 in C_5H_5N); ν_{OH} 3 530 cm^{-1}}.

Methyl 3-O-*benzoyl*-4,6-O-*benzylidene*-α-D-lyxo-*hexopyranosidulose* (9). Molten dicyclohexylcarbodi-imide (1.7 g) and anhydrous phosphoric acid (0.6 g) were added sequentially to a stirred solution of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (3) (10 g) in DMSO (100 ml). After storage for 24 h at ambient temperature, the mixture was treated with oxalic acid dihydrate (10 g). *N,N′*-Dicyclohexylurea oxalate was removed by filtration and was carefully washed sequentially with dilute aqueous sodium hydrogen carbonate and with saturated aqueous sodium chloride. The organic layer of the combined filtrate and washings was dried ($MgSO_4$) and concentrated under reduced pressure. The residue was dissolved in ethyl acetate and the filtered solution was reconcentrated. The residue was crystallised from hot, absolute ethanol to give the *title compound* (8.3 g, 83.5%), m.p. 158 °C; $[\alpha]_D$ +228° (*c*, 0.2); $\nu_{max.}$ 1 765 (CO) and 1 725 cm^{-1} (CO of COPh); δ_H (250 MHz) 8.10—8.20 (2 H, complex m, aromatic protons *ortho* in benzoate residue), 7.33—7.61 (total 8 H, m, ArH), 6.10 (1 H, d, $J_{3,4}$ 4.0 Hz, 3-H), 5.61 (1 H, s, PhC*H*), 4.91 (1 H, s, 1-H), 4.82 (1 H, dd, $J_{4,3}$ 3.7, $J_{4,5}$ 0.7 Hz, 4-H), 4.38 (1 H, dd, $J_{6,6'}$ 12.5, $J_{6,5}$ 1.8 Hz, 6-H), 4.29br (1 H, 5-H), 4.18 (1 H, dd, $J_{6',6}$ 12.5, $J_{6',5}$ 1.5 Hz, 6′-H), and 3.54 (3 H, s, OMe) (Found: C, 65.5; H, 5.3. $C_{21}H_{20}O_7$ requires C, 65.6; H, 5.25%).

Methyl 3-O-*benzoyl*-4,6-O-*benzylidene*-β-D-lyxo-*hexopyranosidulose* (11). The 3-benzoate (6) (8 g) was oxidised in a similar way to that of the α-anomer to afford the β-D-*glycopyranosidulose* (11) (4.5 g, 56%), m.p. 186 °C (from diethyl ether–light petroleum); $[\alpha]_D$ +93.2° (*c*, 0.12); $\nu_{max.}$ 1 760 (CO) and 1 735 cm^{-1} (CO of COPh); δ_H (250 MHz) 8.10—8.14 (2 H, m, aromatic protons *ortho* in benzoate residue), 7.35—7.62 (total 8 H, m, ArH), 5.80 (1 H, dd, $J_{3,4}$ 3.7, $J_{3,1}$ 0.7 Hz, 3-H), 5.60 (1 H, s, PhC*H*), 5.06 (1 H, d, $J_{1,3}$ 0.7 Hz, 1-H), 4.81 (1 H, dd, $J_{4,3}$ 3.7, $J_{4,5}$ 1.5 Hz, 4-H), 4.43 (1 H, dd, $J_{6,6'}$ 12.5, $J_{6,5}$ 1.8 Hz, 6-H), 4.20 (1 H, dd, $J_{6',6}$ 12.5, $J_{6',5}$ 1.8 Hz, 6′-H), 4.07br (1 H, 5-H), and 3.62 (3 H, s, OMe) (Found: C, 65.3; H, 5.3. $C_{21}H_{20}O_7$ requires C, 65.6; H, 5.25%).

Methyl 2-O-*benzoyl*-4,6-O-*benzylidene*-α-D-xylo-*hexopyranosid*-3-*ulose* (10). Methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-galactopyranoside (4) (15 g) was oxidised by the same method as used for the other isomers and yielded the title compound (11.2 g, 75%) as a syrup, $[\alpha]_D$ +231° (*c*, 0.37); $\nu_{max.}$ 1 760 (CO) and 1 725 cm^{-1} (CO of COPh); δ_H 8.3—7.2 (total 10 H, complex m, 2 × Ph), 6.3 (1 H, d, $J_{2,1}$ 7 Hz, 2-H), 5.7 (1 H, s, PhC*H*), 5.5 (1 H, d, $J_{1,2}$ 7 Hz, 1-H), 4.6 (1 H, d, $J_{4,5}$ 2 Hz, 4-H), 4.5—4.0 (total 3 H, complex m, 5-, 6-, and 6′-H), and 3.6 (3 H, s, OMe).

Preparation of Methyl Glycopyranosidulose Arylhydrazones and Methyl Arylazo-hexenosides.—Methyl 3-O-*benzoyl*-4,6-*O*-*benzylidene*-α-D-lyxo-*hexopyranosidulose phenylhydrazone* (12). Methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*lyxo*-hexopyranosidulose (9) (4 g) was dissolved in DMF (20 ml) and a solution of phenylhydrazine (1.1 ml) in glacial acetic acid (0.2 ml) was added. The mixture was stored in the dark for 10 h at room temperature and then ice–water (500 ml) was added to the vigorously stirred mixture. A solid separated and was collected by filtration and dried (P_2O_5, *in vacuo*). Recrystallisation from absolute ethanol afforded the *title compound* (4.2 g, 86%), m.p. 177 °C; $[\alpha]_D$ +224° (*c*, 0.33); $\nu_{max.}$ 3 300, 1 725, 1 600, and 1 500 cm^{-1}; $\lambda_{max.}$ 278 nm (ε 20 856); δ_H 8.2—6.7 (total 16 H, complex m, 3 × Ph and NH), 6.04 (1 H, d, $J_{3,4}$ 4.5 Hz, 3-H), 5.68 (1 H, s, PhC*H*), 5.58 (1 H, s, 1-H), 4.56 (1 H, dd, $J_{4,3}$ 4.5, $J_{4,5}$ 1.5 Hz, 4-H), 4.32 (1 H, dd, $J_{6,6'}$ 12.5, $J_{6,5}$ 1.0 Hz, 6-H), 4.12 (1 H, dd, $J_{6',6}$ 12.5, $J_{6',5}$ 1.5 Hz, 6′-H), 3.98 (1 H, complex m, 5-H), and 3.5 (3 H, s, OMe) (Found: C, 68.1; H, 5.5; N, 5.8. $C_{27}H_{26}N_2O_6$ requires C, 68.3; H, 5.5; N, 5.9%).

Methyl 3-O-*benzoyl*-4,6-O-*benzylidene*-α-D-lyxo-*hexopyranosidulose* 4-*nitrophenylhydrazone* (13). A solution of compound (9) (1 g) in absolute ethanol (10 ml) was added slowly to a stirred solution of 4-nitrophenylhydrazine (0.4 g) in ethanol (5 ml). Glacial acetic acid (0.3 ml) was then added and the mixture was warmed and kept at 45 °C for 30 min. The solution was then cooled slowly and kept at 0 °C for 3 h. The oil which separated was crystallised by the addition of ice–water (40 ml) with stirring of the mixture. Filtration afforded yellow crystals of the *title compound* (1.1 g, 81.5%) which, after recrystallisation from ethanol–water (4 : 1), had m.p. 121 °C; $[\alpha]_D$ +315° (*c*, 0.24); $\nu_{max.}$ 3 350 (NH), 1 730 (COPh), 1 600, and 1 495 cm^{-1}; $\lambda_{max.}$ 378 nm (ε 26 200); δ_H ([$^2H_6$]benzene) 8.25—6.2 [total 15 H, complex m, 2 × Ph, $C_6H_4NO_2$, and NH (exchangeable on D_2O shake)], 5.98 (1 H, d, $J_{3,4}$ 3.5 Hz, 3-H), 5.8 (1 H, s, PhC*H*), 5.3 (1 H, s, 1-H), 4.0—3.6 (total 2 H, complex m, 4- and 6-H), 3.36 (1 H, dd, $J_{6',6}$ 12, $J_{6',5}$ 1.0 Hz, 6′-H), 3.14 (1 H, complex m, 5-H), and 3.0 (3 H, s, OMe) (Found: C, 62.5; H, 4.9; N, 8.0. $C_{27}H_{25}N_3O_8$ requires C, 62.4; H, 4.85; N, 8.1%).

Likewise, *methyl* 3-O-*benzoyl*-4,6-O-*benzylidene*-α-D-lyxo-*hexopyranosidulose* 2,4-*dinitrophenylhydrazone* (14) was prepated from compound (9) (1 g) in DMF (5 ml) and 2,4-dinitrophenylhydrazine (0.52 g) in glacial acetic acid (0.2 ml). After storage in darkness for 8 h the product was isolated as a *yellow powder* (1.4 g, 93%) which was washed with water and dried (P_2O_5, *in vacuo*). The product had m.p. 109 °C; $[\alpha]_D$ +253° (*c*, 0.2); $\nu_{max.}$ 3 300 (NH), 1 710 (CO of COPh), 1 615, and 1 510 cm^{-1}; $\lambda_{max.}$ 350 nm (ε 47 100) (Found: N, 10.6. $C_{27}H_{24}N_4O_{10}$ requires N, 9.9%).

Methyl 3-O-*benzoyl*-4,6-O-*benzylidene*-β-D-lyxo-*hexopyranosidulose* 4-*nitrophenylhydrazone* (15). Compound (11) (1 g) was treated with 4-nitrophenylhydrazine (0.4 g), DMF (8 ml), and glacial acetic acid (0.5 ml) for 15 h. Yellow crystals of the 4-*nitrophenylhydrazone* were obtained (0.92 g, 68%), m.p. 136 °C (from 96% ethanol); $\nu_{max.}$ 3 295 (NH), 1 700 (CO of COPh), 1 600, and 1 510 cm^{-1}; $\lambda_{max.}$ 378 nm; δ_H 8.38 (1 H, s, exchangeable with D_2O, NH), 8.28—6.62 (total 14 H, complex m, 2 × Ph and $C_6H_4NO_2$), 6.06 (1 H, d, $J_{3,4}$ 4 Hz, 3-H), 5.72 (1 H, s, PhC*H*), 5.64 (1 H, s, 1-H), 4.6 (1 H, dd, $J_{4,3}$ 4, $J_{4,5}$ 1.5 Hz, 4-H), 4.44—4.0 (total 2 H, complex m, 6- and 6′-H), 3.96 (1 H, complex m, 5-H), and 3.44 (3 H, s, OMe) (Found: N, 7.9. $C_{27}H_{25}N_3O_8$ requires N, 8.1%).

The analogous 2,4-*dinitrophenylhydrazone* (16) (0.97 g, 66%) was prepared from compound (11) (1 g), 2,4-dinitrophenylhydrazine (0.52 g), DMF (1 ml), and glacial acetic acid (0.5 ml), and was obtained as *orange crystals*, m.p. 128 °C (decomp.); $\nu_{max.}$ 3 300 (NH), 1 705 (CO of COPh), 1 620, 1 580, and 1 520 cm^{-1}; $\lambda_{max.}$ 350 nm (ε 22 500); δ_H ([$^2H_6$]benzene) 9.74—6.66 (total 14 H, complex m, 2 × Ph, $C_6H_3(NO_2)_2$, and NH), 5.34 (1 H, s, PhC*H*), 5.1 (1 H, d, $J_{3,4}$ 4 Hz, 3-H), 5.06 (1 H, s, 1-H), 4.1—3.2 (total 4 H, complex m, 4-, 5-, 6-, and 6′-H), and 3.26 (3 H, s, OMe) (Found: N, 9.8. $C_{27}H_{24}N_4O_{10}$ requires N, 9.9%).

Methyl 2-O-*benzoyl*-4,6-O-*benzylidene*-α-D-xylo-*hexopyranosid*-3-*ulose* 2,4-*dinitrophenylhydrazone* (17). This compound was prepared from methyl 2-*O*-benzoyl-4,6-*O*-benzylidene-α-D-*xylo*-hexopyranosid-3-ulose (10) (1 g), 2,4-dinitrophenylhydrazine (0.52 g), DMF (12 ml), and glacial acetic acid (0.5 ml) according to the procedure described for the preparation of compound (14). Orange-yellow crystals (1.34 g, 91%) of *compound* (17) were obtained, after recrystallisation from ethanol–water (2 : 1), with m.p. 142 °C; $\nu_{max.}$ 3 300 (NH), 1 720 (CO of COPh), 1 615, 1 580, and 1 510 cm^{-1}; $\lambda_{max.}$ 350 nm; δ_H (220 MHz) 9.5—7.6 (total 14 H, complex m, 2 × Ph, $C_6H_3(NO_2)_2$, and NH), 6.25 (1 H, d, $J_{2,1}$ 5.5 Hz, 2-H), 5.81 (1 H, s, PhC*H*), 5.3 (1 H, d, $J_{1,2}$ 5.5 Hz, 1-H), 5.22 (1H, d, $J_{4,5}$ 1.25 Hz, 4-H), 4.55—4.3 (total 2 H, 2 × dd, $J_{6,6'}$ 13, $J_{6,5}$ 1.25 Hz, 6- and 6′-H), 4.07 (1 H, complex m, 5-H), and 3.5 (3 H, s, OMe) (Found: N, 9.9. $C_{27}H_{24}N_4O_{10}$ requires N, 9.9%).

Methyl 4,6-O-*benzylidene*-2,3-*dideoxy*-3-*phenylazo*-α-D-threo-*hex*-2-*enopyranoside* (18). The uloside (10) (5 g) was dissolved in a mixture of DMF (50 ml) and glacial acetic acid (1 ml). Phenylhydrazine (1.3 ml) was added and the mixture was stored for 20 h in the dark at room temperature and was then poured into stirred ice–water (400 ml) and the yellow solid which separated was collected by filtration, washed with water (3 × 50 ml), and dried (P_2O_5, *in vacuo*). The title *phenylazo-compound* (3.9 g, 85%), when recrystallised from 96% ethanol, had m.p. 205 °C; $[\alpha]_D$ −356° (*c*, 0.2); $\lambda_{max.}$ 302 nm (ε 20 240); δ_H 8.27—7.44 (total 10 H, complex m, 2 × Ph), 7.12 (1 H, d, $J_{2,1}$ 4 Hz, 2-H), 5.86 (1 H, s, PhC*H*), 5.68 (1 H, d, $J_{1,2}$ 4 Hz, 1-H), 5.24 (1 H, d, $J_{4,5}$ 2 Hz, 4-H), 4.64 (1 H, dd, $J_{6,5}$ 1.5, $J_{6,6'}$ 13.5 Hz, 6-H), 4.4 (1 H, dd, $J_{6,6'}$ 13.5 Hz, 6′-H), 4.02 (1 H, complex m, 5-H), and 3.66 (3 H, s, OMe) (Found: C, 68.3; H, 5.5; N, 8.05. $C_{20}H_{20}N_2O_4$ requires C, 68.2; H, 5.7; N, 7.95%).

Methyl 4,6-O-*benzylidene*-2,3-*dideoxy*-2-*phenylazo*-α-D-threo-*hex*-2-*enopyranoside* (19). Sodium hydride (0.5 g) in 2-methylpropan-2-ol (20 ml) was added to a solution of the phenylhydrazone (12) (10 g) in DMF (75 ml) at room temperature. The mixture was set aside for 4 h in a dark cupboard and was then poured into stirred ice–water (800 ml). The solid which separated was collected and dried (P_2O_5, *in vacuo*). On recrystallisation from ethanol the *phenylazo-compound* (19) (7 g, 94%) was obtained, m.p. 190 °C; $[\alpha]_D$ −617° (*c*, 0.23); $\lambda_{max.}$ 305 nm; δ_H 8.16—7.26 (total 10 H, complex m, 2 × Ph), 7.16 (1 H, d, $J_{3,4}$ 5 Hz, 3-H), 5.82 and 5.8 (total 2 H, overlapping s, PhC*H* and 1-H), 4.72 (1 H, dd, $J_{3,4}$ 5, $J_{4,5}$ 2 Hz, 4-H), 4.6—4.06 (total 3 H, complex m, 5-, 6-, and 6′-H), and 3.6 (3 H, s, OMe) (Found: C, 67.85; H, 5.7; N, 8.0. $C_{20}H_{20}N_2O_4$ requires C, 68.2; H, 5.7; N, 7.95%).

Methyl 4,6-O-*benzylidene*-2,3-*dideoxy*-2-*phenylazo*-β-D-threo-*hex*-2-*enopyranoside* (20). A solution of methyl 3-*O*-benzoyl-4,6-*O*-benzylidene-β-D-*lyxo*-hexopyranosidulose (11) (2 g) in DMF (10 ml), when treated with phenylhydrazine (0.5 ml) and glacial acetic acid (0.5 ml) for 8 h, afforded the *title compound* (1.34 g, 90%), m.p. 212 °C (from aqueous ethanol); $\lambda_{max.}$ 305 nm; δ_H 7.9—7.26 (total 10 H, complex m, 2 × Ph), 6.94 (1 H, d, $J_{3,4}$ 5.5 Hz, 3-H), 5.68 (total 2 H, PhC*H* and 1-H), 5.64 (1 H, dd, $J_{4,3}$ 5.5, $J_{4,5}$ 2 Hz, 4-H), 4.52—4.16 (total 2 H, complex m, 6- and 6′-H), 4.08 (1 H, complex m, 5-H), and 3.6 (3 H, s, OMe) (Found: C, 68.9; H, 6.2; N, 7.9. $C_{20}H_{20}N_2O_4$ requires C, 68.2; H, 5.7; N, 7.95%).

1,4-*Addition Reactions of the Phenylazo*-α-D-*glycenosides* (18) *and* (19).—(i) *Additions to methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-3-*phenylazo*-α-D-threo-*hex*-2-*enopyranoside* (18). (a) *Benzylamine*. Benzylamine (0.5 ml) was added to a solution of the 3-phenylazo-alkene (18) (0.15 g) in DMF (3 ml). T.l.c. monitoring (solvent *c*) showed that reaction was complete in 2 h and then the mixture was poured into stirred ice–water (10 ml) to yield a pale-yellow solid (0.17 g, 87%) which was collected by filtration, washed with water (3 × 20 ml), and dried (P_2O_5, *in vacuo*). The *methyl* 2-*benzylamino*-4,6-O-*benzylidene*-2-*deoxy*-α-D-lyxo-*hexopyranosid*-3-*ulose phenylhydrazone* (21) so obtained had m.p. 128—130 °C; $\lambda_{max.}$ 284 nm; $\nu_{max.}$ 3 200 and 1 600 cm^{-1}; δ_H 8.56 (1 H, s, NNH), 7.88—6.9 (total 15 H, complex m, 3 × Ph), 5.78 (1 H, s, PhC*H*), 5.14 (1 H, d, $J_{2,1}$ 2 Hz, 1-H), 5.08 (1 H, d, $J_{4,5}$ 2 Hz, 4-H), 4.6—4.12 (total 2 H, 2 × dd, $J_{6,5}$ 2, $J_{6,6'}$ 13 Hz, 6- and 6′-H), 3.98—3.8 (total 2 H, complex m, 2- and 5-H), 3.48 (3 H, s, OMe), 3.26 (2 H, complex m, CH_2Ph), and 2.9br (1 H, s, N*H*CH_2Ph) (Found: C, 70.95; H, 6.6; N, 8.8. $C_{27}H_{29}N_3O_4$ requires C, 70.6; H, 6.3; N, 9.1%).

(b) *Benzenethiol*. Benzenethiol (0.5 ml) and sodium hydride (*ca.* 20 mg) were added sequentially to a solution of the phenylazo-glycenoside (18) (0.2 g) in acetone (5 ml). When the solution was warmed to 40—45 °C for 10 min its orange colour faded to a light-yellow; the reaction was monitored by t.l.c. (solvent *b*) and was shown to be complete. The solvent was evaporated under diminished pressure to give a mixture (0.23 g) of two products. The major component, *methyl* 4,6-O-*benzylidene*-2-*deoxy*-2-*phenylthio*-α-D-lyxo-*hexopyranosid*-3-*ulose phenylhydrazone* (22) (0.18 g, 73%), was separated by crystallisation from diethyl ether. When recrystallised from propan-2-ol–water (5 : 1) it had m.p. 146 °C; $\nu_{max.}$ 3 350 and 1 590 cm^{-1}; $\lambda_{max.}$ 290 nm; δ_H (250 MHz) 8.07 (1 H, s, NH), 6.83—7.67 (total 15 H, m, 3 × Ph), 5.73 (1 H, s, PhC*H*), 5.08 (1 H, d, $J_{1,2}$ 2.2 Hz, 1-H), 4.99 (1 H, d, $J_{2,1}$ 2.2 Hz, 2-H), 4.43 (1 H, dd, $J_{6,6'}$ 12.9 $J_{6,5}$ 1.1 Hz, 6-H), 4.27 [1 H, dd, $J_{6,6'}$ 12.9, $J_{6',5}$ 2.0 Hz (av.), 6′-H], 4.08 (1 H, d, $J_{4,5}$ 2.6 Hz, 4-H), 3.85br (1 H, 5-H), and 3.35 (3 H, s, OMe) (N.B. there is a possibility that the assignments to 2- and 4-H could be interchanged).

(c) *Dimethylamine*. Solutions of compound (18) (0.3 g) in

ethanol (5 ml) and dimethylamine in ethanol (2 ml of a 33% w/v solution) were mixed. The orange colour of the mixture faded rapidly when it was warmed to 50 °C (t.l.c., solvent *c*). The mixture was concentrated to dryness and the solid residue (0.33 g, quantitative) was crystallised from ethanol–water (5 : 1). The product, *methyl* 4,6-O-*benzylidene*-2-*deoxy*-2-*dimethylamino*-α-D-lyxo-*hexopyranosid*-3-*ulose phenylhydrazone* (23), had m.p. 193 °C; $\nu_{max.}$ 3 250 and 1 590 cm^{-1}; $\lambda_{max.}$ 285 nm (Found: C, 66.45; H, 6.9; N, 10.5. $C_{22}H_{27}N_3O_4$ requires C, 66.5; H, 6.85; N, 10.6%).

(d) *Ammonia*. Aqueous ammonia (S.G. 0.88; 1 ml) was added to a solution of the phenylazo-alkene (18) (0.2 g) in ethanol (4 ml). During the time the solution was being stirred over 6 h at room temperature its colour changed from orange to light-yellow and t.l.c. (solvent *d*) showed that the reaction was essentially complete. The solvent was evaporated off and the syrupy residue was dissolved in methanol (5 ml) and acetylated with acetic anhydride (0.7 ml). *Methyl* 2-*acetamido*-4,6-O-*benzylidene*-2-*deoxy*-α-D-lyxo-*hexopyranosid*-3-*ulose phenylhydrazone* (24) (0.21 g, 94%) was obtained in crystalline form on the addition of ice–water (5 ml). The crystals were collected, washed thoroughly with cold water (2 × 20 ml), and dried (P_2O_5, *in vacuo*), m.p. 162 °C; $\nu_{max.}$ 3 270, 1 700, and 1 600 cm^{-1}; $\lambda_{max.}$ 284 nm; δ_H (250 MHz) 9.08 (1 H, s, exchangeable on D_2O shake, NNH), 6.83—7.59 (total 10 H, m, 2 × Ph), 6.54 (1 H, d, $J_{NHAc,2}$ 10 Hz, NHAc), 5.66 (1 H, s, PhCH), 5.03 (1 H, d, $J_{2,NHAc}$ 10 Hz, 2-H), 4.89 (1 H, s, 1-H), 4.60 (1 H, s, 4-H), 4.37 (1 H, dd, $J_{6,6'}$ 12.8, $J_{6,5}$ 1.5 Hz, 6-H), 4.23 [1 H, dd, $J_{6,6'}$ 12.8, $J_{6',5}$ 1.6 Hz (av.), 6′-H], 3.96br (1 H, 5-H), 3.41 (3 H, s, OMe), and 1.92 (3 H, s, NHAc) (Found: N, 9.75. $C_{22}H_{25}N_3O_5$ requires N, 10.2%).

(ii) *Additions to methyl* 4,6-O-*benzylidene*-2,3-*dideoxy*-2-*phenylazo*-α-D-threo-*hex*-2-*enopyranoside* (19). (a) *Methylamine*. A solution of the phenylazo-alkene (19) (0.4 g) in ethanol (10 ml) was treated with a solution of methylamine in ethanol (3 ml of a 33% w/v solution) at reflux temperature for 1 h during which time the deep-yellow colour of the mixture faded. The product was isolated in the customary manner and *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-*methylamino*-α-D-lyxo- (*or* xylo-) *hexopyranosidulose phenylhydrazone* (25) (0.3 g, 69%) was obtained with m.p., 98—99 °C; $\nu_{max.}$ 3 300 and 1 590 cm^{-1}; $\lambda_{max.}$ 281 nm; δ_H ([$^2H_6$]benzene) 8.68 (1 H, s, exchangeable with D_2O, NNH), 7.9—6.98 (total 10 H, m, 2 × Ph), 5.76 (1 H, s, PhCH), 5.64 (1 H, s, 1-H), 4.52 (1 H, dd, $J_{6,6'}$ 13.5, $J_{6,5}$ 1.5 Hz, 6-H), 4.3 (1 H, dd, $J_{6',6}$ 13.5, $J_{6',5}$ 2 Hz, 6′-H), 4.26 (1 H, dd, $J_{4,3}$ 3.5, $J_{4,5}$ 2 Hz, 4-H), 4.02 (1 H, complex m, 5-H), 3.64 (3 H, s, OMe), 3.6 (1 H, d, $J_{3,4}$ 3.5 Hz, 3-H), 2.68 (3 H, s, NMe), and 2.14 (1 H, s, NHMe) (Found: N, 10.3. $C_{21}H_{25}N_3O_4$ requires N, 10.9%).

(b) *Dimethylamine*. A solution of compound (19) (0.5 g) in DMF (10 ml) was treated with a solution of dimethylamine in ethanol (2 ml of a 33% w/v solution) at 45 °C. T.l.c. (solvent *c*) showed that the reaction was complete in 30 min. The dimethylamino-adduct, *methyl* 4,6-O-*benzylidene*-3-*deoxy*-3-*dimethylamino*-α-D-lyxo- (*or* xylo-) *hexopyranosidulose phenylhydrazone* (26), was isolated as a pale-yellow solid (0.24 g, 75%), m.p. 116—118 °C (from ethanol–water, 6 : 1); $\nu_{max.}$ 3 310 and 1 605 cm^{-1}; $\lambda_{max.}$ 282 nm; δ_H ([$^2H_6$]benzene) 9.9 (1 H, s, NNH), 7.64—6.88 (total 10 H, m, 2 × Ph), 5.3 and 5.26 (total 2 H, s and 2 overlapping s, PhCH and 1-H), 4.06 (1 H, dd, $J_{6,6'}$ 13, $J_{6,5}$ 2 Hz, 6-H), 3.8 (1 H, dd, $J_{4,5}$ 1.5, $J_{4,3}$ 1 Hz, 4-H), 3.68 (1 H, m, 5-H), 3.54 (1 H, d, $J_{3,4}$ 1 Hz, 3-H), 3.24 (1 H, dd, $J_{6,6'}$ 13, $J_{6',5}$ 1.5 Hz, 6′-H), 3.1 (3 H, s, OMe), and 2.0 (6 H, s, NMe_2) (Found: C, 66.7; H, 7.0. $C_{22}H_{27}N_3O_4$ requires C, 66.5; H, 6.85%).

(c) *Benzylamine*. The procedure used to prepare compound (21) was adopted to give the benzylamino-adduct, *methyl* 3-*benzylamino*-4,6-O-*benzylidene*-3-*deoxy*-α-D-lyxo- (*or* xylo-) *hexopyranosidulose phenylhydrazone* (27) (0.19 g, 73%), from the phenylazo-alkene (19) (0.2 g) and benzylamine (1 ml) in DMF (4 ml). The adduct had m.p. 132—134 °C; $\nu_{max.}$ 3 290 and 1 560 cm^{-1}; $\lambda_{max.}$ 283 nm (Found: C, 71.2; H, 6.7; N, 8.4. $C_{27}H_{29}N_3O_4$ requires C, 70.6; H, 6.3; N, 9.1%).

(d) *Sodium borohydride*. Sodium borohydride (0.03 g) was added to a solution of compound (19) (0.2 g) in methanol (6 ml). T.l.c. (solvent *c*) indicated that the reaction was complete in 2 h. *Methyl* 4,6-O-*benzylidene*-3-*deoxy*-α-D-threo-*hexopyranosidulose phenylhydrazone* (28) (0.15 g, 74%) was isolated and recrystallised from aqueous propan-2-ol. It had m.p. 65—66 °C; $\nu_{max.}$ 3 290 and 1 590 cm^{-1}; $\lambda_{max.}$ 281 nm; δ_H 8.28 (1 H, s, NH), 7.96—7.0 (total 10 H, m, 2 × Ph), 5.8 (1 H, s, 1-H), 5.74 (1 H, s, PhCH), 4.6—3.52 (total 4 H, complex m, 4-, 5-, 6-, and 6′-H), and 3.04 and 2.98 (total 5 H, 2 overlapping s, 3-H_2 and OMe) (Found: N, 7.3. $C_{20}H_{22}N_2O_4$ requires N, 7.9%).

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