Purines, Pyrimidines, and Imidazoles. Part 57.[1] Reactions of Some Oxazolino-xylofuranose Derivatives

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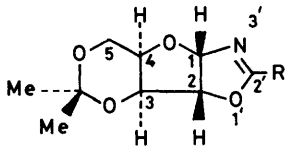
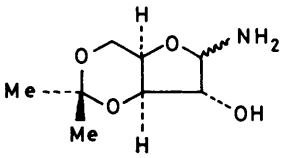
2'-Methyl-3,5-*O*-isopropylidene-α-D-xylofuranoso[1,2-*d*]-Δ$^{2'}$-oxazoline reacts with benzaldehyde, *p*-nitrobenzaldehyde, and anisaldehyde to give 2'-styryl-, 2'-*p*-nitrostyryl-, or 2'-*p*-methoxystyryl-3,5-*O*-isopropylidene-α-D-xylofuranoso[1,2-*d*]-Δ$^{2'}$-oxazolines. 3,5-*O*-Isopropylidene-D-xylofuranosylamine with carbon disulphide gave 2'-mercapto-3,5-*O*-isopropylidene-α-Δ-xylofuranoso[1,2-*d*]-Δ$^{2'}$-oxazoline, methylation of which produced the 2'-methylthio-oxazoline, which was desulphurised to give 3,5-*O*-isopropylidene-α-D-xylofuranoso[1,2-*d*]-Δ$^{2'}$-oxazoline. The xylosylamine with *p*-tolylsulphonylaminoacetimidate and benzyloxycarbonylaminoacetimidate gave 2'-*p*-tolylsulphonylaminomethyl (or benzyloxycarbonylaminomethyl)-3,5-*O*-isopropylidene-α-D-xylofuranoso[1,2-*d*]-Δ$^{2'}$-oxazolines respectively. The tolylsulphonylaminomethyl-oxazoline with hydrogen sulphide gave 3,5-*O*-isopropylidene-*N*-(*N*-*p*-tolylsulphonylthioglycyl)-D-xylofuranosylamine which with methanesulphonyl chloride gave 3,5-*O*-isopropylidene-2'-(*p*-tolylsulphonylaminomethyl)-α-D-xylofuranoso[1,2-*d*]-Δ$^{2'}$-thiazoline. Reaction of the *p*-tolylsulphonylaminomethyl- or benzyloxycarbonylaminomethyl-oxazolines with hydroxylamine gave corresponding 3,5-*O*-isopropylidene-D-xylofuranosylamidoximes, whereas with ammonia the sugar unit was cleaved and simple glycinamidines obtained. The structures assigned were confirmed by analytical, u.v., n.m.r., and mass-spectral techniques.

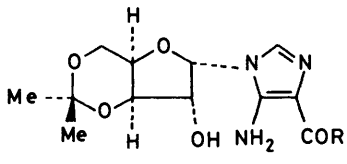
In an earlier part of this series [2] we described the preparation of a novel α-D-xylofuranoso[1,2-*d*]-Δ$^{2'}$-oxazoline (1a)† by the reaction of 3,5-*O*-isopropylidene-D-xylofuranosylamine [3] (2) with either ethyl formimidate,



(1) a; R = H
b; R = Me
c; R = CH=CHPh
d; R = CH=CHC$_6$H$_4$NO$_2$-*p*
e; R = CH=CHC$_6$H$_4$Me-*p*
f; R = SH
g; R = SMe
h; R = CH$_2$NHSO$_2$C$_6$H$_4$Me-*p*
i; R = CH$_2$NHCO$_2$CH$_2$Ph
j; R = CH$_2$Ph



(2)



(3) a; R = OEt
b; R = NH$_2$

formamidine, or dimethylformamide dimethyl acetal. The oxazoline has proved to be a valuable intermediate for the stereospecific synthesis of α-D-xylofuranosyl aminoimidazoles. Thus reaction of (1a) with ethyl α-amino-α-cyanoacetate or α-amino-α-cyanoacetamide gave the α-D-xylofuranosyl amino-imidazole ester (3a) and carboxamide (3b) respectively. Derivatives of this type are also valuable intermediates for the synthesis of related purine nucleosides by well established cyclisation reactions. We wished to extend these reactions to include carbohydrates other than xylose and to examine the general chemistry of this new type of oxazoline sugar.

RESULTS AND DISCUSSION

The methyl group in the 2-methyloxazoline (1b), prepared from the xylosylamine (2) and ethyl acetimidate, was reactive. Thus with benzaldehyde and an iodine catalyst the styryloxazolino-derivative (1c) was obtained in high yield, and similar derivatives (1d) and (1e) were prepared from the appropriate aldehydes. However, the styryl derivatives were much less active than the original derivative (1b) and when heated with ethyl α-amino-α-cyanoacetate, they failed to give amino-imidazole nucleosides.

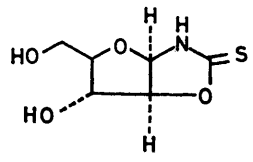
When the xylosylamine (2) was treated with carbon disulphide and potassium hydroxide the 2-mercapto-oxazoline (1f) was obtained as a crystalline solid. The structure assigned to the compound was confirmed by elemental analysis and n.m.r. spectroscopy. In addition, however, the i.r. spectrum of the compound showed the presence of a strong band at 1 485 cm^{-1}, suggesting that the compound exists largely in the thione rather than the thiol form.

Similar compounds have been reported [4] to result from the reaction of several carbohydrates with potassium thiocyanate and hydrochloric acid, but these compounds were earlier assigned an isomeric oxazoline structure in which the nitrogen atom is sited at the 2-position of the carbohydrate. However, recently [5] the structure of the arabinothionoxazolidine (4) was confirmed by its use as

† The IUPAC name for the unsubstituted ring-system (1) is 3a,8a,3b,7b-tetrahydro-5*H*,7*H*-dioxino[5',4':2,3]furo[2,3-*d*]-[1,3]oxazoline.

an intermediate in a new synthesis of 9-β-D-arabinofuranosyladenine. The synthesis involved a nitroarylation of (4) which in the presence of mercuric bromide produced the *N*-aryl derivative, whereas in the absence of the mercury salt an *S*-aryl derivative was obtained.

Reaction of the oxazoline (1f) with methyl iodide and base in alcohol produced the crystalline *S*-methyl derivative (1g) in high yield. The structure assigned to the latter compound was confirmed by desulphurisation with Raney nickel in hot benzene to produce the oxazoline (1a). However, both the mercapto-oxazoline (1f) or the *S*-methyl derivative (1g) failed to produce amino-imidazoles when heated with ethyl α-amino-α-cyano-acetate. The methylthio-derivative was singularly unreactive towards nucleophiles; thus it was recovered



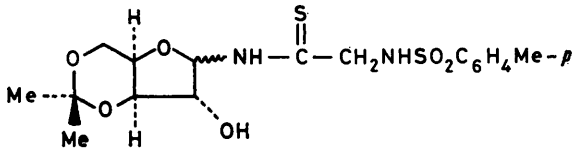
(4)

$RNHCH_2C(=NH)COEt$

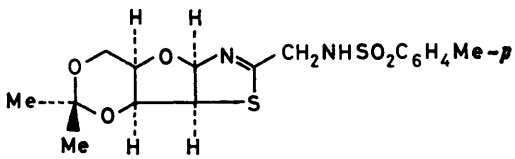
(5) a; $R = SO_2C_6H_4Me\text{-}p$
b; $R = CO{-}OCH_2Ph$

unchanged after heating with ammonia at 100 °C in a sealed tube.

Apart from their use as a source of amino-imidazole nucleosides the oxazolino-sugars are a potential source of acyclic nucleosides related to natural intermediates in purine nucleotide biosynthesis, including glycyl, substituted glycyl, and glycinamidine derivatives. Reaction of the tolylsulphonylamino-acetimidate [6] (5a) with the xylosylamine (2) readily gave a good yield of the crystalline oxazoline (1h) and the similarly protected



(6)

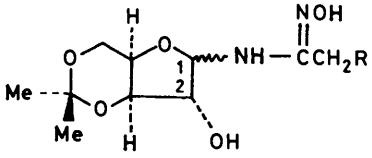


(7)

benzyloxycarbonylamino-acetimidate [6] (5b) produced the oxazoline (1i). The structures of the compounds were confirmed by elemental analysis, i.r. spectroscopy [with strong bands at 1 620 cm^{-1} (C=N) and 1 380 cm^{-1} (CMe_2)], and n.m.r. spectra which were similar to those of the other oxazolino-derivatives examined. Treatment of the tosyl derivative (1h) with hydrogen sulphide smoothly produced the crystalline tosylaminothioacetamido-derivative (6), the structure of which was confirmed by elemental analysis, mass and i.r. spectra, and by its conversion into the novel thiazoline (7) with methanesulphonyl chloride or toluene-*p*-sulphonyl chloride in pyridine. The thiazoline, from its mode of formation, presumably has the D-*lyxo*-configuration.

$R^1NHCH_2C(=NH)NHR^2$

(8) a; $R^1 = SO_2C_6H_4Me\text{-}p$, $R^2 = H$
b; $R^1 = CO{-}OCH_2Ph$, $R^2 = H$
c; $R^1 = SO_2C_6H_4Me\text{-}p$,
R^2 = 3, 5-*O*-isopropylidene-D-xylofuranosyl
d; $R^1 = CO{-}OCH_2Ph$,
R^2 = 3, 5-*O*-isopropylidene-D-xylofuranosyl



(9) a; $R = NHSO_2C_6H_4Me\text{-}p$
b; R = Ph

The oxazolines (1h) and (1i) with ammonia, however, produced the amidines [6] (8a) and (8b), respectively, in which the xyloxyl moiety has been cleaved from the intermediate glycinamidines (8c) and (8d), which were presumably first formed. However, reaction of the oxazoline (1h) with hydroxylamine resulted in retention of the sugar and formation of the β-amidoxime derivatives (9a), and a similar mixture of anomers (9b) was readily produced from the 2-benzyloxazoline (1j), which was prepared from (2) and ethyl 2-phenylacetimidate.

EXPERIMENTAL

Evaporations were carried out with a Büchi rotary evaporator under water-pump vacuum with a flask temperature ⩽40 °C unless otherwise stated. U.v. absorption spectra were measured with a Unicam SP 800 spectrophotometer, i.r. spectra with a Perkin-Elmer 157 spectrophotometer, n.m.r. spectra with a JEOL-MH-100 spectrometer (tetramethylsilane or 3-trimethylsilylpropane-1-sulphonic acid as internal standard), and mass spectra with an A.E.I. MS 902 spectrometer. Silica gel (0.05—0.20 mm; 315—70 mesh) from Machery Nagel and Co. was used for column chromatography, and silica gel $60F_{254}$ 0.25-mm pre-coated glass plates from Merck were used for t.l.c. with (A) $CHCl_3$–MeOH (9 : 1), and (B) butanol–acetic acid–water (12 : 3 : 5) as development systems.

3,5-O-*Isopropylidene-2'-styryl-α-*D-*xylofuranoso*[1,2-d]-$\Delta^{2'}$-*oxazoline* (1c).—A mixture of 3,5-*O*-isopropylidene-2'-methyl-α-D-xylofuranoso[1,2-*d*]-$\Delta^{2'}$-oxazoline (1.0 g), benzaldehyde (0.5 g), and a crystal of iodine in dry toluene (5 ml) was refluxed for 1 h. The cooled solution was diluted

with chloroform (30 ml), washed with 0.5N-sodium hydroxide (30 ml), dried (Na_2SO_4), and evaporated to a solid which was collected and washed with toluene. The *styryl-oxazoline* (1.1 g) recrystallised from toluene as needles, m.p. 206—208 °C (Found: C, 67.9; H, 6.20; N, 4.36. $C_{17}H_{19}NO_4$ requires C, 67.75; H, 6.35; N, 4.65%); δ 6.34 (H-1, d, $J_{1,2}$ 6 Hz) 1.46 (CMe_2), and 6.64 (CH=CH, d, 16 Hz); $\lambda_{max.}$ 285 nm (ε 25 700) in MeOH.

3,5-O-*Isopropylidene*-2′-p-*nitrostyryl*-α-D-*xylofuranoso*-[1,2-d]-Δ²′-*oxazoline* (1d).—The 2′-methyloxazoline (1.0 g), *p*-nitrobenzaldehyde (0.71 g), and a crystal of iodine in dry toluene (5 ml) similarly gave the p-*nitrostyryloxazoline* (0.5 g), which crystallised from toluene as yellow needles, m.p. 196—198 °C (Found: C, 59.0; H, 5.1; N, 8.0. $C_{17}H_{18}N_2O_6$ requires C, 58.95; H, 5.25; N, 8.1%); $\lambda_{max.}$ 308 nm (ε 28 000) in MeOH.

3,5-O-*Isopropylidene*-2-p-*methoxystyryl*-α-D-*xylofuranoso*-[1,2-d]-Δ²′-*oxazoline* (1e).—The 2′-methyloxazoline (1.0 g), *p*-methoxybenzaldehyde (0.64 g), and a crystal of iodine in dry toluene (5 ml) produced the p-*methoxystyryloxazoline* (0.6 g), which crystallised from toluene as fine needles, m.p. 150—152 °C; $\lambda_{max.}$ 313 nm (ε 35 000) in MeOH (Found: C, 65.4; H, 6.6; H, 4.2. $C_{18}N_{21}NO_5$ requires C, 65.25; H, 6.4; N, 4.25%).

3,5-O-*Isopropylidene*-2-*mercapto*-α-D-*xylofuranoso*[1,2-d]-Δ²′-*oxazoline* (1f).—To a cooled solution of 3,5-*O*-isopropylidene-D-xylofuranosylamine toluene-*p*-sulphonate [2] (7.2 g) in water (25 ml) containing a solution of potassium hydroxide (5.0 g) in water (25 ml) was added a solution of carbon disulphide (1.52 g) in dioxan (40 ml), and the resulting solution stirred rapidly for 5 min. To the now orange solution was added a solution of potassium hydroxide (5 g) in water (100 ml) followed by a solution of lead nitrate (6.62 g) in water (150 ml). The dark brown mixture was then warmed in a water-bath at 60 °C for 1 h, cooled, and filtered. The filtrate was evaporated to *ca.* 100 ml and adjusted to pH 7 with 2N-hydrochloric acid, and then extracted with chloroform (3 × 50 ml). The organic phase was dried (Na_2SO_4) and evaporated to a gum. A solution of this in ethanol soon gave a crystalline solid. The *mercapto-oxazoline* (0.5 g) was recrystallised from ethanol as needles, m.p. 189—190 °C (Found: C, 47.0; H, 5.8; N, 5.95; S, 13.55. $C_9H_{13}NO_4S$ requires C, 46.75; H, 5.65; N, 6.05; S, 13.9%).

A further quantity of the oxazoline (0.1 g) was produced by chromatography of the mother-liquors on silica gel; δ 5.96 (H-1); $\lambda_{max.}$ 244 nm (ε 13 100) in MeOH; $\nu_{max.}$ 1 485 cm^{-1} (C=S).

3,5-O-*Isopropylidene*-2′-*methylthio*-α-D-*xylofuranoso*[1,2-d]-Δ²′-*oxazoline* (1g).—To a solution of the foregoing 2-mercapto-oxazoline (0.5 g) in aqueous ethanol (1 : 2) (30 ml) containing sodium hydroxide (0.05 g) was added iodomethane (0.35 g) with shaking. The solution was set aside for 3 h, water (30 ml) added, then extracted with chloroform (3 × 20 ml). The organic phase was dried (Na_2SO_4) and evaporated to a clear syrup which soon crystallised. The *methylthio-oxazoline* (0.39) recrystallised slowly from ethanol as large prisms, m.p. 118—120 °C (Found: C, 48.9; H, 6.2; N, 5.75; S, 12.8. $C_{10}H_{15}NO_4S$ requires C, 48.95; H, 6.15; N, 5.7; S, 13.1%); δ 6.10 (H-1, d, $J_{1,2}$ 6 Hz), 1.46 (CMe_2), and 2.50 (SMe, s); $\lambda_{max.}$ 217 nm (ε 4 800) in MeOH.

A solution of the 2-methylthio-oxazoline (0.5 g) and ethyl α-amino-α-cyanoacetate [7] (0.22 g) in dry methanol (10 ml) was refluxed for 15 min, during which time a strong smell of methanethiol was noticed. T.l.c. examination (system A) showed the presence of several Bratton–Marshall active spots which were identical with the products of the self-condensation of ethyl α-amino-α-cyanoacetate.[8]

A suspension of the 2-methylthio-oxazoline (0.2 g) in dry methanol (20 ml) saturated with ammonia was heated in a sealed tube to 100 °C for 2 h. The solution was evaporated to a solid (0.1 g) identical with the starting material (m.p., mixed m.p., i.r.).

3,5-O-*Isopropylidene*-α-D-*xylofuranoso*[1,2-d]-Δ²′-*oxazoline* (1a).—A solution of the foregoing methylthio-oxazoline (0.2 g) in dry benzene (15 ml) with Raney Nickel (3 g) was stirred and refluxed for 2 h, then filtered and the nickel washed with hot benzene (3 × 10 ml). The combined filtrates were evaporated to a clear gum which soon crystallised. The product (0.05 g) was identical with 3,5-*O*-isopropylidene-α-D-xylofuranoso[1,2-*d*]-Δ²′-oxazoline [2] (m.p., mixed m.p., i.r.).

3,5-O-*Isopropylidene*-2′-N-p-*tolylsulphonylaminomethyl*-α-D-*xylofuranoso*[1,2-d]-Δ²′-*oxazoline* (1h).—A suspension of powdered 2-*N*-*p*-tolylsulphonylaminoacetimidate hydrochloride (3 g) in a solution of 3,5-*O*-isopropylidene-D-xylofuranosyl toluene-*p*-sulphonate (3.6 g) and sodium (0.23 g) in ethanol (50 ml) was shaken at room temperature for 2 h, when the mixture suddenly solidified. It was dissolved in chloroform (40 ml) and this solution washed with water (2 × 50 ml). The organic layer was dried (Na_2SO_4) and evaporated to a yellow solid, which crystallised with ethanol. The *oxazoline* (1.8 g) recrystallised from chloroform–ethanol (1 : 3) as needles (Found: C, 53.85; H, 5.65; N, 7.3; S, 8.2. $C_{17}H_{22}N_2O_6S$ requires C, 53.4; H, 5.8; N, 7.35; S, 8.35%); δ 6.1 (H-1, d, $J_{1,2}$ 6 Hz) and 1.4 (CMe_2); $\lambda_{max.}$ 227 nm (ε 16 800) in MeOH; $\nu_{max.}$ 1 620 cm^{-1} (C=N) and 1 380 cm^{-1} (CMe_2). Dry ammonia was bubbled into a cooled suspension of the oxazoline (0.5 g) in methanol (15 ml) until a 10% increase in weight was achieved. After 6 h the solution was evaporated to low volume and dry ether added to give a white precipitate of 2-*N*-*p*-tolylsulphonylglycinamidine (0.3 g), m.p. 177—178 °C (lit.,[6] m.p. 179—180 °C) identical with an authentic sample.

3,5-O-*Isopropylidene*-2′-N-*benzyloxycarbonylaminomethyl*-α-D-*xylofuranoso*[1,2-d]-Δ²′-*oxazoline* (1i).— A suspension of powered 2-*N*-benzyloxycarbonylaminoacetimidate hydrochloride (3 g) in a solution of 3,5-*O*-isopropylidene-D-xylofuranosylamine toluene-*p*-sulphonate (3.6 g), triethylamine (1.4 ml), and acetonitrile (40 ml) was shaken at room temperature for 1 h. The precipitate was removed and the filtrate evaporated to a gum. A solution of the gum in chloroform (30 ml) was washed with water (20 ml), dried (Na_2SO_4), and again evaporated and the residue in ethyl acetate made turbid with light petroleum (b.p. 40—60 °C) to precipitate a solid. The *oxazoline* (1 g) was recrystallised from ethyl acetate as needles, m.p. 147—149 °C (Found: C, 59.65; H, 6.05; N, 7.75. $C_{18}H_{22}N_2O_6$ requires C, 59.65; H, 6.1; N, 7.75%); $\lambda_{max.}$ 209 nm (ε 6 000) in MeOH; $\nu_{max.}$ 1 620 cm^{-1} (C=N) and 1 380 cm^{-1} (CMe_2). With dry ammonia as above, 2-(*N*-benzyloxycarbonylamino)glycinamidine, m.p. 134—136 °C (lit.,[6] 137—139 °C), was obtained, identical with an authentic specimen.

3,5-O-*Isopropylidene*-N-(N-p-*tolylsulphonylthioglycyl*)-α- *or* β-D-*xylofuranosylamine* (6).—A suspension of the foregoing 2′-*p*-tolylsulphonylaminomethyloxazoline (1 g) in a mixture of chloroform (15 ml), ethanol (50 ml), and triethylamine (6 ml) was saturated with hydrogen sulphide. The solid slowly dissolved, to leave a clear yellow solution. After 5 h the solution was evaporated to a yellow solid foam.

This crystallised with ethanol. The *thioglycylxylosylamine* (0.9 g) was recrystallised from ethanol as needles, m.p. 192—194 °C (Found: C, 48.9; H, 5.75; N, 6.7; S, 15.2. $C_{17}H_{24}N_2O_6S_2$ requires C, 49.05; H, 5.8; N, 6.75; N, 67.75; S, 15.4%); δ 6.0, 6.22 (α-H-1, β-H-1, $J_{\alpha1,2}$ 4, $J_{\beta1,2}$ 6 Hz) and 1.34 (CMe_2); $\lambda_{max.}$ 228 and 270 nm (ε 10 900, 10 000) in MeOH.

3,5-O-*Isopropylidene-2'-(p-tolylsulphonylaminomethyl)-α-D-xylofuranoso*[1,2-d]-$\Delta^{2'}$-*thiazoline* (7).— To a solution of the foregoing *p*-tolylsulphonylthioglycylxylofuranosylamine (0.3 g) in dry pyridine (15 ml) cooled to −10 °C was added methanesulphonyl chloride (0.12 g) dropwise, with stirring, during a few minutes. The solution was stood at 0 °C for 20 h, then poured into an ice–water (100 ml) mixture and extracted with chloroform (3 × 30 ml). The extract was washed with saturated sodium hydrogencarbonate solution (30 ml) and water (30 ml), dried (Na_2SO_4), and evaporated to a gum which solidified with ethyl acetate. The *thiazoline* (0.12 g) crystallised from ethanol–chloroform as small prisms, m.p. 209—210 °C (Found: C, 51.5; H, 5.4; N, 6.85; S, 15.9. $C_{17}H_{22}N_2O_5S_2$ requires C, 51.25; H, 5.55; N, 7.05; S, 16.1%). The same compound was obtained when toluene-*p*-sulphonyl chloride was used; δ 5.8 ($J_{1'\,2'}$ 6 Hz) and 1.38 (CMe_2); $\lambda_{max.}$ 230 nm (ε 4 500) in MeOH.

N-(3,5-O-*Isopropylidene-D-xylofuranosyl*)-2-(p-*tolylsulphonylamino*)*acetamidoxime* (9a).—To a solution of the foregoing *p*-tolylsulphonylaminomethyl-oxazoline in chloroform (10 ml) was added a solution of sodium (0.023 g) and finely powdered hydroxylammonium chloride (0.06 g) in ethanol (20 ml) with shaking. The mixture was stood overnight then filtered and evaporated to a solid, which was extracted with hot chloroform (3 × 15 ml) and the extract evaporated to dryness. The *amidoxime* (0.2 g) crystallised from ethanol as needles, m.p. 166—169 °C (Found: C, 49.05, H, 5.95; N, 9.95; S, 7.7. $C_{17}H_{25}N_3O_7S$ requires C, 49.15; H, 6.05; N, 10.1; S, 7.7%); $\lambda_{max.}$ 223 nm (ε 12 900) in MeOH; δ 1.32 (CMe_2) and 9.72 (NOH).

3,5-O-*Isopropylidene-2'-benzyl-α-D-xylofuranoso*[1,2-d]-$\Delta^{2'}$-*oxazoline* (1j).—Ethyl phenylacetimidate hydrochloride (2.0 g) was added to a solution of 3,5-*O*-isopropylidene-D-xylofuranosylamine toluene-*p*-sulphonate (3.6 g) and triethylamine (1.0 g) in acetonitrile (60 ml) and the mixture shaken at room temperature for 1 h. The solution was filtered and the filtrate evaporated to a gum; this was dissolved in chloroform (60 ml), washed with 0.5N-sodium hydroxide (30 ml), dried (Na_2SO_4), and evaporated to a gum. A solution of the residue in ethyl acetate soon crystallised on the careful addition of light petroleum (b.p. 40—60 °C). The oxazoline (1.2 g) was recrystallised from the same solvents as needles, m.p. 130—132 °C (Found: C, 66.6; H, 6.7; N, 4.75%; *m/e* 290. $C_{19}H_{19}NO_4$ requires C, 66.45; H, 6.6; N, 4.85%; *M*, 289).

N-(3',5'-O-*Isopropylidene-α or β-D-xylofuranosyl*)-2-*phenylacetamidoxime* (9b).—The foregoing benzyloxazoline (0.6 g) in chloroform (10 ml) with sodium (0.046 g) and finely powdered hydroxylammonium chloride (0.40 g) in ethanol (20 ml) was set aside at room temperature overnight, and then filtered. The filtrate was evaporated to a solid which was extracted with hot ethanol (3 × 15 ml), and the combined extracts evaporated to a solid. The *amidoxime* (0.35 g) was recrystallised from ethanol as fine needles, m.p. 189—190 °C (Found: C, 59.85; H, 6.85; N, 8.85%; M^+, 322. $C_{16}H_{22}N_2O_5$ requires C, 59.6; H, 6.9; N, 8.7%; *M*, 322); δ 6.14, 6.2 [H_α-1, H_β-1, $J_{\alpha1',2'}$ 4, $J_{\beta1',2'}$ 10 Hz) and 1.32 (CMe_2); $\lambda_{max.}$ 214 nm (ε 8 500) in MeOH.

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