Oxidation of Enamines Derived from Sugars

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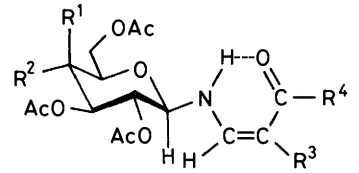
The oxidation of sugar enamines with $KMnO_4$–$NaIO_4$ has been studied. The products depend on the extent of substitution of the enaminic double bond. For 2′-monosubstituted enamines, *N*-formyl or *N*-acyl amino sugars are obtained, whereas the 2,2′-disubstituted substrates afforded α-hydroxy amides, together with those products of double-bond cleavage. *Z*–*E* Isomerism in the *N*-formyl amino sugars has been observed.

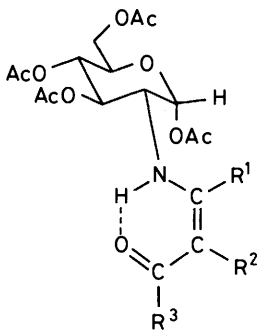
Enamines derived from sugars are synthetically available by several methods, including the reaction of amino sugars with β-dicarbonyl compounds,[1–3] enol ethers,[4–7] and active acetylenic compounds.[8,9] These substances have been used to prepare polyhydroxyalkyl heterocycles[1,10] and also in processes that involve protection of the amino group.[4–7,11] In addition, the oxidation of enamines is well documented[12,13] and is useful for the synthesis of a variety of structures (depending on the type of the substitution at the double bond and on the oxidizer); however, for enamines derived from sugars, as far as we are aware, there are no precedents. In this paper, we account for our first results in this field.

The starting compounds have been the acetylated enamines (**1**)—(**7**) that have different patterns of substitution at the double bond and on the sugar ring. They all had been prepared previously (see Experimental section) except in the case of (**3**), which was obtained from D-glucopyranosylamine and benzoylacetaldehyde. As oxidizers we used the systems $KMnO_4$–$NaIO_4$/acetone–water, $KMnO_4$/acetone–water, and $NaIO_4$–RuO_2/chloroform–water; the best results were obtained with the first system. Thus, oxidation of C-2′-disubstituted enamines (**1**), (**2**), and (**4**) afforded mixtures of α-hydroxy amides (**8**), (**9**), and (**10**) and *N*-formyl amino sugars (**11**), (**12**), and (**13**), the latter being minor products. Alternatively, the C-2′-monosubstituted enamines (**3**), (**5**), (**6**), and (**7**) gave only *N*-formyl (**11**), (**13**), or *N*-acetyl (**14**) amino sugars in moderate yields.

The structures proposed for the new compounds were demonstrated by elemental analyses and spectral data; so, for compounds (**3**), (**8**), (**9**), (**11**), and (**12**), the β-anomeric configuration in the $^4C_1$ (D) conformation is consistent with the large values of $J_{1,2}$ (8.3—10.0 Hz). For compounds (**10**) and (**13**), the values of $J_{1,2}$ (~3.5 Hz) together with those of $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ (9.0—10.4 Hz) support the α-anomeric configuration in the $^4C_1$ (D) conformation. The coupling constant (8.0 Hz) between the olefinic protons in substrate (**3**) indicates a *Z* configuration for the double bond. The hydroxy group in the α-hydroxy amides appears as a D_2O-exchangeable singlet at 4.76—5.06 p.p.m. For all compounds described, the large couplings $J_{NH,1}$ or $J_{NH,2}$ are in agreement with an *anti*-periplanar disposition between the corresponding protons. In the ^1H and ^{13}C n.m.r. spectra (recorded in 0.1M $CDCl_3$ solutions at room temperature) of *N*-formyl derivatives (**11**), (**12**), and (**13**), we observe a duplication of the signals, those corresponding to the *Z* isomer being the more intense (*E*/*Z* ratio 3:1). In the case of *E* isomers the signal of the formyl proton appears as a doublet ($J_{NH,CHO}$ ~ 10 Hz), whereas for *Z* isomers this signal is a singlet[14] ($J_{NH,CHO}$ ~ 0 Hz) at slightly lower field. We note also that the proton on the carbon that supports the amide group resonates at lower field for *Z* isomers than for *E* isomers (Δδ 0.6—0.7 p.p.m.); this fact could be due to a deshielding effect of the carbonyl group on this proton, nearer in the *Z* isomers. On the other hand, in ^{13}C n.m.r. spectra, the carbons adjacent to NH are at lower field for the *E* isomers.

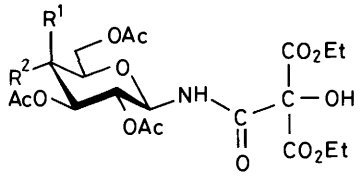


(**1**) R^1 = H, R^2 = OAc, R^3 = CO_2Et, R^4 = OEt
(**2**) R^1 = OAc, R^2 = H, R^3 = CO_2Et, R^4 = OEt
(**3**) R^1 = R^3 = H, R^2 = OAc, R^4 = Ph

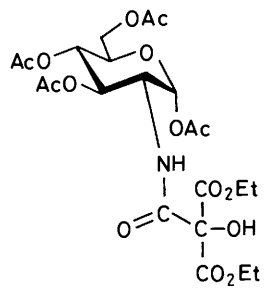


(**4**) R^1 = H, R^2 = CO_2Et, R^3 = OEt
(**5**) R^1 = Me, R^2 = H, R^3 = OMe
(**6**) R^1 = R^3 = Me, R^2 = H
(**7**) R^1 = R^2 = H, R^3 = Ph

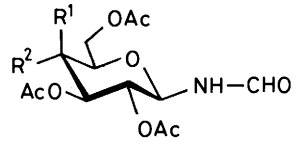
The *N*-formyl amino sugars, which had been previously obtained by more tedious methods than we propose here, are synthetic intermediates in the preparation of isocyanides.[15–17] Moreover, *N*-formyl amino sugars are present in a variety of interesting natural products, as in some antigenic polysaccharides of *Brucella abortus* and *B. melitensis*,[18–20] and in other polysaccharide residues of *Vibro cholerae* and *Pseudomonas aeruginosa*.[21,22] The α-hydroxy amides could be related to biological substances such as the 'Lipid A' of *Salmonellae* and



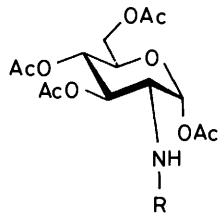
(**8**) R^1 = H, R^2 = OAc
(**9**) R^1 = OAc, R^2 = H



(**10**)



(**11**) R^1 = H, R^2 = OAc
(**12**) R^1 = OAc, R^2 = H



(**13**) R = CHO
(**14**) R = Ac

Escherichia coli,[23] nucleosides such as gougerotin,[24] and sugars such as *N*-acylkansosamine, the primary cell-wall inmunodeterminant of *Mycobacterium kansasii*.[25]

Experimental

General Methods.—M.p.s were determined using a Gallenkamp apparatus and are uncorrected. Optical rotations were measured at 20 ± 2 °C with a Perkin-Elmer 141 polarimeter. U.v. and i.r. spectra were recorded using Beckman DU-50 and Perkin-Elmer 399 spectrophotometers, respectively. ^{1}H N.m.r. (200.13 MHz) and ^{13}C n.m.r. (50.33 MHz) were obtained on Bruker AC 200 E or Varian XL-200 instruments; chemical shifts (p.p.m.) are reported relative to Me_4Si as internal standard. T.l.c. was performed on silica gel (Merck GF_{254}) and flash column chromatography on silica gel Merck 60 (230—400 mesh); solvents were (a) light petroleum–acetone–chloroform (3:2:1); (b) light petroleum–ethyl acetate (2:1); and (c) benzene–ethanol–ether (3:1:1) where light petroleum refers to the fraction boiling in the range 40—60 °C.

2,3,4,6-*Tetra*-O-*acetyl*-N-[(Z)-2-*benzoylvinyl*]-β-D-*glucopyranosylamine* (**3**).—A mixture of D-glucopyranosylamine[26] (3.53 g, 19.53 mmol), methanol (60 ml), triethylamine (0.1 ml), and benzoylacetaldehyde (3.75 g, 25.36 mmol) was stirred for 24 h at room temperature. The solvent was then evaporated off and the residue was subjected to column chromatography (solvent b) to eliminate unchanged benzoylacetaldehyde. Further elution with solvent c afforded almost pure *N*-[(*Z*)-2-benzoylvinyl]-β-D-glucopyranosylamine as an amorphous solid (4.0 g) (R_F 0.30, solvent c), which was acetylated in the conventional manner [pyridine (24 ml), acetic anhydride (12 ml)], yielding the *title product* (**3**) (4.9 g, 46%), which was recrystallized from ethanol, m.p. 195—196 °C; $[\alpha]_D$ −40°, $[\alpha]_{578}$ −41°, $[\alpha]_{546}$ −48°, $[\alpha]_{436}$ −104° (*c* 0.5, $CHCl_3$); $\nu_{max.}$(KBr) 3 440w (NH), 3 015w (Ph), 1 740s (CO ester), 1 630s (CO ketone), 1 570m, and 1 540m cm^{-1} (C=C–NH); $\lambda_{max.}$(EtOH) 251 (ε 55 200) and 322 nm (ε 19 000); δ_H($CDCl_3$) 2.03 (6 H, s, 2 OAc), 2.04 (3 H, s, OAc), 2.19 (3 H, s, OAc), 3.79 (1 H, ddd, 5-H), 4.12 (1 H, dd, $J_{5,6'}$ 2.2 Hz, 6-H′), 4.26 (1 H, dd, $J_{5,6}$ 4.4, $J_{6,6'}$ 12.4 Hz, 6-H), 4.52 (1 H, t, $J_{1,2}$ 9.6 Hz, 1-H), 5.12 (1 H, t, $J_{3,4}$ 9.3 Hz, 4-H), 5.14 (1 H, t, 2-H), 5.31 (1 H, t, $J_{2,3}$ = $J_{3,4}$ = 9.3 Hz, 3-H), 5.91 (1 H, d, NHCH=C*H*), 6.92 (1 H, dd, $J_{1',2'}$ 8.0 Hz, NHC*H*=CH), 7.42—7.89 (3 H, m, Ph), 7.89 (2 H, m, Ph), and 10.26 (1 H, dd, $J_{NH,1}$ 8.9, $J_{NH,1'}$ 11.3 Hz, NH; addition of D_2O caused disappearance of this signal, and those at δ 4.52 and 6.92 collapsed to doublets); δ_C($CDCl_3$) 20.6, 20.8 (OCO*C*H$_3$), 61.9 (C-6), 68.2, 70.5 (C-4, -2), 72.9 (C-3), 73.7 (C-5), 86.7 (C-1), 94.4 (NHCH=*C*H), 127.5, 128.4, 131.7, 139.0 (Ph), 150.1 (NH*C*H=CH), 169.4, 169.5, 170.2, 170.7 (O*C*OCH$_3$), and 191.3 (*C*OPh) (Found: C, 58.1; H, 5.8; N, 3.1. $C_{23}H_{27}NO_{10}$ requires C, 57.85; H, 5.70; N, 2.93%).

General Procedure for the Oxidation of the Enamines (**1**)—(**7**).—To a solution of the enamine (3.86 mmol) in acetone–water (1:1; 40 ml) were added potassium permanganate (0.73 g, 4.63 mmol) and potassium metaperiodate (1.06 g, 4.63 mmol). The mixture was stirred at room temperature until t.l.c. (solvent a, detection with u.v. light and 50% H_2SO_4) showed disappearance of starting enamine * (2—3 h). The resulting MnO_2 was filtered off, and thoroughly washed with acetone, the filtrate and washings were evaporated, and the mixture was extracted with chloroform (4 × 30 ml). The organic layer was dried over anhydrous $MgSO_4$, and the solvent was evaporated off.

Oxidation of Diethyl (2,3,4,6-*Tetra*-O-*acetyl*-β-D-*glucopyranosylamino*)*methylenemalonate* (**1**).[4]—Oxidation of compound (**1**) by the general procedure described above led, after work-up, to a residue which was chromatographed on a column of silica gel (solvent a), eluting first *diethyl hydroxy*(2,3,4,6-*tetra*-O-*acetyl*-β-D-*glucopyranosylcarbamoyl*)*malonate* (**8**), which, after evaporation of the solvent, crystallized spontaneously in a desiccator; recrystallized from ether–light petroleum (47% yield), it had m.p. 100—101 °C, $[\alpha]_{578}$ +15°, $[\alpha]_{546}$ +19°, $[\alpha]_{436}$ +33°, $[\alpha]_{365}$ +55° (*c* 0.5, $CHCl_3$); $\nu_{max.}$(KBr) 3 350m (OH, NH), 1 725s (CO ester), 1 660m, and 1 500m cm^{-1} (amide); δ_H($CDCl_3$) 1.33 (6 H, t, *J* 7.1 Hz, 2 × CH$_2$*Me*), 2.03, 2.04, 2.05, 2.09 (each 3 H, each s, 4 × OAc), 3.83 (1 H, ddd, $J_{5,6}$ 4.1, $J_{5,6'}$ 2.1 Hz, 5-H), 4.09 (1 H, dd, $J_{6,6'}$ 12.5 Hz, 6-H′), 4.30 (1 H, dd, 6-H), 4.32 (4 H, m, 2 × C*H*$_2$Me), 4.76 (1 H, s, D_2O-exchangeable, OH), 5.02 (1 H, dd, 2-H), 5.10 (1 H, t, $J_{4,5}$ 9.6 Hz, 4-H), 5.26 (1 H, t, $J_{1,2}$ = $J_{NH,1}$ = 9.9 Hz, 1-H), 5.33 (1 H, t, $J_{2,3}$ = $J_{3,4}$ = 9.5 Hz, 3-H), and 7.76 (1 H, d, NH; addition of D_2O caused disappearance of this signal, and that at δ 5.26 collapsed to a doublet); δ_C($CDCl_3$) 13.7 (CH$_2$*C*H$_3$), 20.4, 20.5, 20.6 (OCO*C*H$_3$), 61.5 (C-6), 63.4, 63.7 (*C*H$_2$Me), 67.9 (C-4), 70.1 (C-2), 72.5 (C-3), 73.7 (C-5), 78.4 (C-1), 79.8 (COH), 165.0 (NHCO), 165.9, 166.1 (*C*O$_2$Et), 169.4, 169.8, 170.5, and 170.6 (O*C*OCH$_3$) (Found: C, 48.2; H, 5.8; N, 2.3. $C_{22}H_{31}NO_{15}$ requires C, 48.09; H, 5.69; N, 2.55%).

Further elution of the column led to 2,3,4,6-*tetra*-O-*acetyl*-N-*formyl*-β-D-*glucopyranosylamine* (**11**) which was recrystallized from ethanol (15% yield), m.p. 147—148 °C; $[\alpha]_{578}$ +21°, $[\alpha]_{546}$ +25°, $[\alpha]_{436}$ +42°, $[\alpha]_{365}$ +68° (*c* 0.5, $CHCl_3$); $\nu_{max.}$(KBr) 3 340m (NH), 1 725s (CO ester), 1 665m, and 1 490m cm^{-1} (amide); δ_H($CDCl_3$; *Z* isomer) 2.02, 2.06, 2.08, 2.10 (each 3 H, each s, 4 × OAc), 3.85 (1 H, ddd, 5-H), 4.10 (1 H, dd, $J_{5,6'}$ 2.1 Hz, 6-H′), 4.35 (1 H, dd, $J_{5,6}$ 4.8, $J_{6,6'}$ 13.1 Hz, 6-H), 4.98 (1 H, t, 2-H), 5.08 (1 H, t, $J_{4,5}$ 9.6 Hz, 4-H), 5.33 (1 H, t, $J_{1,2}$ 9.6 Hz, 1-H), 5.36 (1 H, t, $J_{2,3}$ = $J_{3,4}$ = 9.6 Hz, 3-H), 6.51 (1 H, d, $J_{NH,1}$ 9.3 Hz, NH; addition of D_2O caused disappearance of this signal, and that at δ 5.33 collapsed to a doublet), and 8.26 (1 H, s, $J_{NH,CHO}$ ~ 0 Hz, CHO); δ_H($CDCl_3$; *E* isomer) 2.02—2.11 (12 H, 4 × OAc), 3.81 (1 H, ddd, 5-H), 4.12 (1 H, dd, $J_{5,6'}$ 2.1 Hz, 6-H′), 4.28 (1 H, dd, $J_{5,6}$ 4.8, $J_{6,6'}$ 13.1 Hz, 6-H), 4.73 (1 H, t, $J_{1,2}$ 9.6 Hz,

* If t.l.c. indicates that the reaction is incomplete, additional potassium permanganate and potassium metaperiodate may be added and the oxidation allowed to proceed further.

1-H), 5.02 (1 H, t, 2-H), 5.10 (1 H, t, $J_{4,5}$ 9.6 Hz, 4-H), 5.31 (1 H, t, $J_{2,3} = J_{3,4} = 9.5$ Hz, 3-H), 6.42 (1 H, t, $J_{NH,1}$ 10.5 Hz, NH; addition of D_2O caused disappearance of this signal, and those at δ 4.73 and 8.22 collapsed, respectively, to a doublet and a singlet), and 8.22 (1 H, d, $J_{NH,CHO}$ 10.5 Hz, CHO); δ_C($CDCl_3$; *Z* isomer) 20.5, 20.6, 20.7 ($OCOCH_3$), 61.7 (C-6), 68.1 (C-4), 70.4 (C-2), 72.7, 73.7 (C-3, -5), 76.5 (C-1), 161.2 (NHCO), 169.4, 169.6, 170.7, and 170.9 ($OCOCH_3$); δ_C($CDCl_3$; *E* isomer) 20.5—20.7 ($OCOCH_3$), 61.8 (C-6), 68.0 (C-4), 70.1 (C-2), 72.6, 73.7 (C-3, -5), 81.9 (C-1), 163.6 (NHCO), and 169.4—170.9 ($OCOCH_3$) (Found: C, 48.0; H, 5.7; N, 3.5. $C_{15}H_{21}NO_{10}$ requires C, 48.00; H, 5.64; N, 3.73%).

Oxidation of Diethyl (2,3,4,6-*Tetra*-O-*acetyl*-β-D-*galactopyranosylamino*)*methylenemalonate* (**2**).[4]—Oxidation of compound (**2**) as described for (**1**) gave first (column chromatography, solvent a) *diethyl hydroxy*(2,3,4,6-*tetra*-O-*acetyl*-β-D-*galactopyranosylcarbamoyl*)*malonate* (**9**) as an amorphous solid (52% yield), $[\alpha]_{578}$ +26°, $[\alpha]_{546}$ +30°, $[\alpha]_{436}$ +52°, $[\alpha]_{365}$ +84° (*c* 0.5, $CHCl_3$); $\nu_{max.}$(KBr) 3 340m (OH, NH), 1 740s (CO ester), and 1 510 cm^{-1} (amide); δ_H($CDCl_3$) 1.35 (6 H, t, *J* 7.2 Hz, 2 × CH_2Me), 2.04, 2.09, 2.12, 2.24 (each 3 H, each s, 4 × OAc), 4.16 (3 H, m, 5-H and 6-H_2), 4.40 (4 H, m, 2 × CH_2Me), 5.06 (1 H, s, D_2O-exchangeable, OH), 5.2—5.4 (3 H, m, 1-, 2-, and 3-H), 5.50 (1 H, d, $J_{3,4}$ 0.5, $J_{4,5}$ ~0 Hz, 4-H), and 7.80 (1 H, d, $J_{NH,1}$ 8.9 Hz, D_2O-exchangeable, NH); δ_C($CDCl_3$) 13.5 (CH_2CH_3), 20.2, 20.3 ($OCOCH_3$), 60.8 (C-6), 63.0, 63.3 (CH_2Me), 66.3 (C-4), 67.6 (C-2), 70.4 (C-5), 72.2 (C-3), 78.4 (C-1), 79.7 (COH), 164.8 (NHCO), 165.3, 165.9 (CO_2Et), 168.5, 168.8, 170.0, and 170.5 ($OCOCH_3$) (Found: C, 48.0; H, 5.8; N, 2.6. $C_{22}H_{31}NO_{15}$ requires C, 48.09; H, 5.69; N, 2.55%).

The second compound eluted was 2,3,4,6-*tetra*-O-*acetyl*-N-*formyl*-β-D-*galactopyranosylamine* (**12**); recrystallized from acetone–ether (18% yield), it had m.p. 167—169 °C; $[\alpha]_{578}$ +35°, $[\alpha]_{546}$ +39°, $[\alpha]_{436}$ +68°, $[\alpha]_{365}$ +113° (*c* 0.5, $CHCl_3$); $\nu_{max.}$(KBr) 3 230m, 3 180m (NH), 1 730s (CO ester), 1 660m, and 1 530m cm^{-1} (amide); δ_H($CDCl_3$; *Z* isomer) 2.01, 2.06, 2.08, 2.16 (each 3 H, each s, 4 × OAc), 3.97—4.17 (3 H, m, 5-H and 6-H_2), 5.12—5.17 (2 H, m, 2- and 3-H), 5.31 (1 H, t, $J_{1,2}$ 8.3 Hz, 1-H), 5.45 (1 H, d, $J_{3,4}$ 0.5, $J_{4,5}$ ~0 Hz, 4-H), 6.41 (1 H, d, $J_{NH,1}$ 8.3 Hz, NH; addition of D_2O caused disappearance of this signal, and that at δ 5.31 collapsed to a doublet), and 8.23 (1 H, s, CHO); δ_H($CDCl_3$; *E* isomer) 2.0—2.2 (12 H, 4 × OAc), 3.97—4.17 (3 H, m, 5-H and 6-H_2), 4.67 (1 H, t, $J_{1,2}$ 9.3 Hz, 1-H), 5.12—5.41 (2 H, m, 2- and 3-H), 5.45 (1 H, d, 4-H), 6.23 (1 H, t, $J_{NH,1}$ 9.2 Hz, NH; addition of D_2O caused disappearance of this signal, and those at δ 4.67 and 8.20 collapsed, respectively, to a doublet and a singlet), and 8.20 (1 H, d, $J_{NH,CHO}$ 9.2 Hz, CHO); δ_C($CDCl_3$; *Z* isomer) 20.5, 20.6, 20.7 ($OCOCH_3$), 61.1 (C-6), 67.1 (C-4), 68.1 (C-2), 70.7, 72.5 (C-3, -5), 76.9 (C-1), 160.9 (NHCO), 169.9, 170.0, 170.4, and 171.3 ($OCOCH_3$); δ_C($CDCl_3$; *E* isomer) 20.5—20.7 ($OCOCH_3$), 61.2 (C-6), 66.8 (C-4), 67.6 (C-2), 70.7, 72.4 (C-3, -5), 82.3 (C-1), 163.9 (NHCO), and 169.9—171.3 ($OCOCH_3$) (Found: C, 47.7; H, 5.7; N, 3.5. $C_{15}H_{21}NO_{10}$ requires C, 48.00; H, 5.64; N, 3.73%).

Oxidation of 1,3,4,6-*Tetra*-O-*acetyl*-2-*deoxy*-2-{1-[2,2-*bis*(*ethoxycarbonyl*)*vinyl*]*amino*}-α-D-*glucopyranose* (**4**).[4]—Oxidation of compound (**4**) as described for (**1**) gave first (column chromatography, solvent a) 1,3,4,6-*tetra*-O-*acetyl*-2-*deoxy*-2-[2-*hydroxy*-2,2-*bis*(*ethoxycarbonyl*)*acetamide*]-α-D-*glucopyranose* (**10**), which was crystallized from diethyl ether; recrystallized from diethyl ether (42% yield), the product had m.p. 117—118 °C, $[\alpha]_{578}$ +69°, $[\alpha]_{546}$ +78°, $[\alpha]_{436}$ +126°, $[\alpha]_{365}$ +183° (*c* 0.5, $CHCl_3$); $\nu_{max.}$(KBr) 3 430m, 3 330m (OH, NH), 1 765s, 1 740s, 1 715s (CO ester), 1 690m, 1 520m, and 1 300m cm^{-1} (amide); δ_H($CDCl_3$) 1.30 (6 H, t, *J* 7.2 Hz, 2 × CH_2Me), 2.02, 2.04, 2.09, 2.22 (each 3 H, each s, 4 × OAc), 4.06 (2 H, m, 5-H and 6-H′), 4.29 (5 H, m, 6-H and 2 × CH_2Me), 4.48 (1 H, ddd, 2-H), 5.20 (1 H, t, $J_{4,5}$ 10.4 Hz, 4-H), 5.36 (1 H, t, $J_{2,3} = J_{3,4}$ = 10.4 Hz, 3-H), 6.20 (1 H, d, $J_{1,2}$ 3.5 Hz, 1-H), 7.21 (1 H, d, $J_{NH,2}$ 9.3 Hz, NH; addition of D_2O caused disappearance of this signal, and that at δ 4.48 collapsed to a double doublet); δ_C($CDCl_3$) 13.4 (CH_2CH_3), 20.2, 20.3, 20.4 ($OCOCH_3$), 51.3 (C-2), 61.1 (C-6), 63.0—63.2 (CH_2Me), 67.1 (C-4), 69.4, 69.6 (C-3, -5), 79.3 (COH), 89.5 (C-1), 164.4 (NHCO), 165.9, 166.2 (CO_2Et), 168.3, 168.9, 170.3, and 170.7 ($OCOCH_3$) (Found: C, 48.4; H, 5.8; N, 2.4. $C_{22}H_{31}NO_{15}$ requires C, 48.09; H, 5.69; N, 2.55%).

The second compound eluted was 1,3,4,6-*tetra*-O-*acetyl*-2-*deoxy*-2-*formamide*-α-D-*glucopyranose* (**13**); recrystallized from diethyl ether (28% yield), it had m.p. 129—130 °C; $[\alpha]_{578}$ +93°, $[\alpha]_{546}$ +106°, $[\alpha]_{436}$ +173°, $[\alpha]_{365}$ +253° (*c* 0.5, $CHCl_3$); $\nu_{max.}$(KBr) 3 180m (NH), 1 740s, 1 730s (CO ester), 1 660m, 1 640m, and 1 535m cm^{-1} (amide); δ_H($CDCl_3$; *Z* isomer) 2.05, 2.06, 2.09, 2.19 (each 3 H, each s, 4 × OAc), 4.02 (1 H, m, 5-H), 4.07 (1 H, dd, 6-H′), 4.27 (1 H, dd, $J_{5,6}$ 4.1, $J_{6,6'}$ 12.6 Hz, 6-H), 4.56 (1 H, td, $J_{1,2}$ 3.7, $J_{2,3} = J_{NH,2}$ = 9.6 Hz, 2-H), 5.21 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.6 Hz, 4-H), 5.30 (1 H, t, 3-H), 5.94 (1 H, d, $J_{NH,2}$ 9.6 Hz, NH; addition of D_2O caused disappearance of this signal, and that at δ 4.56 collapsed to a double doublet), 6.19 (1 H, d, 1-H), and 8.14 (1 H, s, CHO); δ_H($CDCl_3$; *E* isomer) 2.05—2.22 (12 H, 4 OAc), 3.80 (1 H, td, $J_{1,2}$ 3.7, $J_{2,3} = J_{NH,2}$ = 9.4 Hz, 2-H), 3.99—4.10 (2 H, m, 5-H and 6-H′), 4.33 (1 H, dd, $J_{5,6}$ 4.5, $J_{6,6'}$ 12.4 Hz, 6-H), 5.16 (1 H, t, $J_{3,4} = J_{4,5}$ = 9.4 Hz, 4-H), 5.21 (1 H, t, 3-H), 6.15 (1 H, t, NH; addition of D_2O caused disappearance of this signal, and those at δ 3.80 and 8.03 collapsed, respectively, to a doublet and a singlet), and 8.03 (1 H, d, $J_{NH,CHO}$ 9.4 Hz, CHO); δ_C($CDCl_3$; *Z* isomer) 20.1, 20.2, 20.3 ($OCOCH_3$), 48.8 (C-2), 61.2 (C-6), 67.3 (C-4), 69.4 (C-5), 69.8 (C-3), 89.8 (C-1), 160.8 (NHCO), 168.5, 168.8, 170.3, and 170.6 ($OCOCH_3$); δ_C($CDCl_3$; *E* isomer) 20.1—20.3 ($OCOCH_3$), 53.5 (C-2), 61.2 (C-6), 67.3 (C-4), 69.3 (C-5), 70.1 (C-3), 90.4 (C-1), 163.6 (NHCO), and 169.1, 169.7, 170.2 ($OCOCH_3$) (Found: C, 47.7; H, 5.75; N, 3.6. $C_{15}H_{21}NO_{10}$ requires C, 48.00; H, 5.64; N, 3.73%).

Oxidation of 2,3,4,6-*Tetra*-O-*acetyl*-N-(2-*benzoylvinyl*)-β-D-*glucopyranosylamine* (**3**).—Oxidation of compound (**3**) by the general procedure led to an oil, which was repeatedly evaporated with ether to yield a white solid; recrystallized from ethanol (47% yield), it showed identical data with those recorded for compound (**11**), described above.

Oxidation of 1,3,4,6-*Tetra*-O-*acetyl*-2-[(2-*benzoylvinyl*)-*amino*]-2-*deoxy*-α-D-*glucopyranose* (**7**).—Oxidation of compound (**7**) by the general procedure afforded a solid (51% yield) that showed identical data with those recorded for compound (**13**), described above.

Oxidation of 1,3,4,6-*Tetra*-O-*acetyl*-2-*deoxy*-2-[(2-*methoxycarbonyl*-1-*methylvinyl*)*amino*]-α-D-*glucopyranose*[28] (**5**).—Oxidation of compound (**5**) as described for (**1**) gave, after column chromatography (solvent a), a solid, which was recrystallized from diethyl ether (35% yield); it showed identical data with those recorded for the previously described[29] 2-acetamido-1,3,4,6-tetra-*O*-acetyl-2-deoxy-α-D-glucopyranose (**14**).

Oxidation of 1,3,4,6-*Tetra*-O-*acetyl*-2-[(2-*acetyl*-1-*methylvinyl*)*amino*]-2-*deoxy*-α-D-*glucopyranose*[30] (**6**).—Oxidation of compound (**6**) as described for (**5**) gave the previously described[29] product (**14**) (31% yield).

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