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SYNTHESES OF (2-NITROVINYL)AMINO SUGARS AND 2- AND 3-(ALDITOL-1-YL)-4-NITROPYRROLES*,†

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ABSTRACT

Reactions of 2-amino-2-deoxy-D-glucose and its *N*-butyl derivative with 1-ethoxy-2-nitroethene produced 2-deoxy-2-[(2-nitrovinyl)amino]-D-glucose (**6**) and its *N*-butyl derivative (**8**), respectively, in high yields. The spectra of these compounds indicated that they were α,β-anomeric mixtures, and also that **6** existed as equilibrium mixtures of the *Z*- and *E*-geometrical isomers, the proportions of which depended on the polarity of the medium. Acetylation of **6** and **8** afforded the corresponding tetra-acetates **7** and **9**. The reaction of β-D-glucopyranosylamine with 1-ethoxy-2-nitroethene yielded syrupy 1-(β-D-glucopyranosylamino)-2-nitroethene, which was characterised as the crystalline tetra-*O*-acetyl derivative. Compounds **6** and **8** cyclised readily to give the 4-nitro-2-(D-*arabino*-tetritol-1-yl)pyrroles **12** and **14**, which could also be obtained by treatment of 2-amino-2-deoxy-D-glucose and its *N*-butyl derivative with 1-ethoxy-2-nitroethene in boiling methanol. Similar reactions with 1-amino-1-deoxy-D-fructose and its *N*-methyl, *N*-butyl, and *N*-*p*-tolyl derivatives afforded the respective 4-nitro-3-(D-*arabino*-tetritol-1-yl)pyrroles. A series of 4-nitro-3- and -2-pyrrolecarbaldehydes was obtained by periodate oxidation of the 2- and 3-(alditol-1-yl)-4-nitropyrroles.

INTRODUCTION

1-Amino-2-nitroalkenes ("nitroenamines") have attracted interest because of their pharmacological properties[2,3] and utility as precursors of heterocyclic compounds[4]. We have described[1,5] the synthesis and properties of 1-alkyl(aryl)amino-2-nitroalkenes and their conversion into imidazoles. Furthermore, α-aminoketones (*e.g.*, **1**) react with 1-ethoxy-2-nitroethene (ENE, **2**) and with α-nitroketones to afford 3-nitropyrroles (*e.g.*, **4**) in high yields[6]. The reaction has been supposed to proceed *via* nitroenamine intermediates (*e.g.*, **3**), the intramolecular aldehyde–enamine condensation of which affords the pyrroles. The similar synthesis of 3-acyl-

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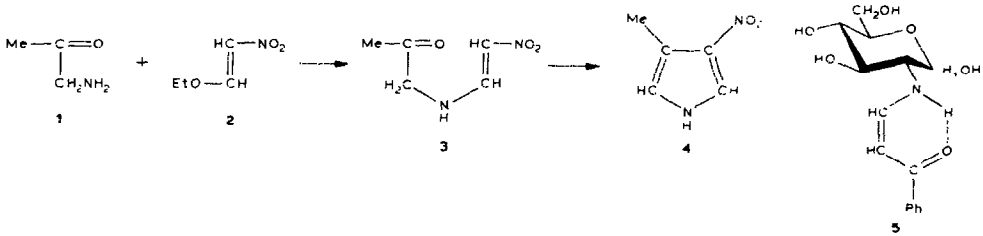
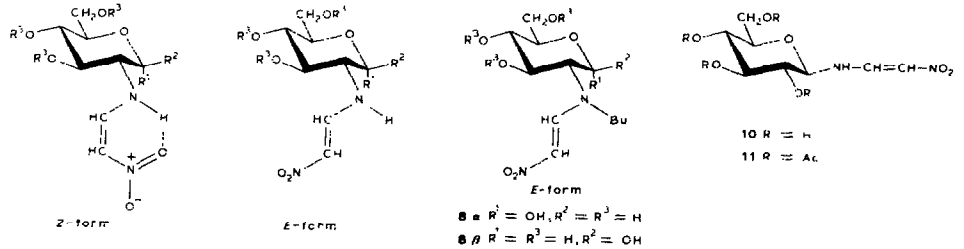
pyrroles by reaction of α-amino-aldehydes and -ketones (including the amino sugars) with 1,3-dicarbonyl compounds is well documented[7,8]. In these cases, the enamine intermediates (*e.g.*, **5**) can be easily isolated. We now report on the reaction of amino sugars with ENE to yield 2- and 3-(alditol-1-yl)-4-nitropyrroles; some of the anticipated intermediate nitroenamines have been isolated. Many nitropyrroles possess antimicrobial activity[9], and some 3-(alditol-1-yl)-4-nitropyrroles have been prepared[10] in order to test their biological properties. These compounds are usually obtained by nitration of other pyrroles, but the procedure has the disadvantage of producing mixtures of isomers and the further complexity derived from side reactions[11]; yields of the desired products are usually low.



RESULTS AND DISCUSSION

Treatment of 2-amino-2-deoxy-D-glucose and its *N*-butyl derivative with an equimolecular amount of ENE in methanol at 0° afforded almost quantitative yields of **6** and **8**, respectively, as amorphous, unstable solids which could not be crystallised. Their acetylation (acetic anhydride–pyridine) gave (>80%) the corresponding crystalline tetra-acetates **7** and **9**. Compounds **6–9** were chromatographically homogeneous, but their spectral properties (see below) indicated that they were α,β-anomeric mixtures; **6** and **7** existed as equilibrium mixtures of the *Z*- and *E*-forms, the proportion of which depended on the polarity of the medium, whereas the tertiary nitroenamines **8** and **9** were always in the less-hindered *E*-configuration. The acetate **7α** was obtained pure by column chromatography of the mixture **7α** + **7β**. Evidence for these structures is as follows.



6 α $R^1 = OH, R^2 = R^3 = H$
6 β $R^1 = R^3 = H, R^2 = OH$
7 α $R^1 = OAc, R^2 = H, R^3 = Ac$
7 β $R^1 = H, R^2 = OAc, R^3 = Ac$

8 α $R^1 = OH, R^2 = R^3 = H$
8 β $R^1 = R^3 = H, R^2 = OH$
9 α $R^1 = OAc, R^2 = H, R^3 = Ac$
9 β $R^1 = H, R^2 = OAc, R^3 = Ac$

10 R = H
11 R = Ac

TABLE I

I.R. ABSORPTIONS (cm^{-1}) FOR COMPOUNDS **6–9** AND **11**

Compound	*Medium*	*ν(OH)*	*ν(N–H)*		*ν(C=C) + δ(N–H)*		$\nu_{as}(NO_2)$	*AcO*
			Z	E	Z	E		
6	KBr	3400s,br	(a)		1640s		1464m	
7	KBr			3430w		1622s	1486m	1738s
								1724s
	$CDCl_3$		3005w[b]		1642s		1498m	1755s
	$(CD_3)_2SO$				1643s	1624s	1475sh	1755s
8	KBr	3460s,br				1610s	1482m	
9	KBr					1616s	1487s	1748s
11	KBr		3305w[b]		1645s		1501w	1757s
							1486w	
	$CDCl_3$		3220w[b]		1649m		1512w	1757s
	$(CD_3)_2SO$				1645m,sh	1625m	1470w	1755s

[a]Overlapped by the ν(OH) absorption. [b]Intramolecularly bonded N–H.

The i.r. absorptions (Table I) indicated the presence of the nitroenamine system, and the geometric configurations were assigned by comparison with the spectra of the *Z*- and *E*-forms of simple 1-(alkylamino)-2-nitroethenes[1,12,13]. A more detailed i.r. study indicated that solid **7** existed in the *E*-form, whereas, in solution in $CDCl_3$, it adopted exclusively the *Z*-configuration; in solution in the more polar $(CD_3)_2SO$, it was an equilibrium mixture of both forms. The geometric isomers and the anomeric forms of **6–9** could be better distinguished by their n.m.r. spectra (Table II). In the *E*-form, H-1′ is strongly deshielded by the *cis*-NO_2 group and its signal appeared at lower field (δ 8.1–8.4) than for the *Z*-form (δ 6.6–7.3); the $J_{1',2'}$ values were ~11 Hz and ~6 Hz, respectively. Furthermore, the H-1′ signal for the α-anomer appeared at lower field than for the β-anomer. The ^{13}C signals of the sugar moiety were assigned by comparison with the spectra of 2-amino-2-deoxy-α,β-D-glucopyranose[14] and its *N*-acetyl derivative[15]. The data showed that **6** existed in D_2O solution as a ~4:1 mixture of the α-*Z*- and α-*E*-isomers; in CD_3OD, the α,β-ratio was ~3:2. Compounds **7α** and **7β** had the *Z*-configuration in $CDCl_3$. In CD_3OD, **8** was in the *E*-form as a ~2:1 α,β-anomeric mixture, and the acetates **9α** and **9β** also had the *E*-configuration in $CDCl_3$.

Treatment of β-D-glucopyranosylamine with ENE yielded syrupy 1-(β-D-glucopyranosylamino)-2-nitroethene (**10**), which was readily transformed into the crystalline tetra-*O*-acetyl derivative **11**. The spectral data of **11** (see Table I and Experimental) indicated that it also existed either in the *Z*- or the *E*-form, or as a mixture of the two, depending on the conditions.

When the reactions of 2-amino- and 2-butylamino-2-deoxy-D-glucose with ENE were performed in boiling methanol, the main products were the nitropyrroles **12** and **14**, respectively, isolated as amorphous solids and characterised as

TABLE II

N.M.R. DATA[a] (δ, p.p.m.; J, Hz) FOR **6–9**

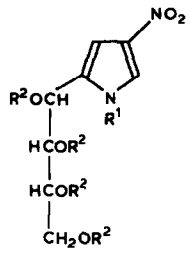
Nucleus	*Compounds*								
	6α,Z[b]	**6α,E**[b]	**6β,E**[c]	**7α,Z**	**7β,Z**	**8α,E**	**8β,E**	**9α,E**	**9β,E**
H-1	5.28d	5.36d		6.27d	5.94d			6.27d	5.86d
	$J_{1,2}$ 3.3	$J_{1,2}$ 3.3		$J_{1,2}$ 3.8	$J_{1,2}$ 8.3			$J_{1,2}$ 3.4	$J_{1,2}$ 8.7
H-2				3.68dt	3.45q			3.64dd	3.49t,br
				$J_{2,3}$ 10.0	$J_{2,3}$ 9.4			$J_{2,3}$ 11.3	$J_{2,3}$ 10.5
				$J_{NH,2}$ 9.5					
H-3				5.40t	5.49t			5.64dd	5.44dd
				$J_{3,4}$ 10.0	$J_{3,4}$ 9.4			$J_{3,4}$ 9.1	$J_{3,4}$ 9.2
H-4				5.14t	5.12t			5.18t	5.12t
				$J_{4,5}$ 10.0	$J_{4,5}$ 9.4			$J_{4,5}$ 10	$J_{4,5}$ 10
H-5				4.1m	3.97–4.47m			3.93m	3.93ddd
H-6a				4.35dd	3.97–4.47m			4.34dd	4.34dd
				$J_{5,6a}$ 4.0				$J_{5,6a}$ 4.1	$J_{5,6a}$ 4.4
				$J_{6a,6b}$ 12.6				$J_{6a,6b}$ 12.6	$J_{6a,6b}$ 12.6
H-6b				4.1m	3.97–4.47m			4.14dd	4.11dd
								$J_{5,6b}$ 2.3	$J_{5,6b}$ 2.1
NH				8.69dd	8.06bt				
				$J_{NH,1}$ 13.2					
H-1′	7.30d	8.43d		6.66dd	6.59dd	8.31d	8.11d	8.25d	8.06d
	$J_{1',2'}$ 6.0	$J_{1',2'}$ 11.3		$J_{1',2'}$ 6.0	$J_{1',2'}$ 6.0	$J_{1',2'}$ 10.8	$J_{1',2'}$ 10.8	$J_{1',2'}$ 11.3	$J_{1',2'}$ 11.1
H-2′	6.70d	7.31d		6.44d	6.40d	6.84d	6.79d	6.58d	6.62d
AcO				2.26s	2.13s				2.20s, 2.15s, 2.09s,
				2.09s	2.07s				2.04s, 2.02s
				2.05s	2.04s				
C-1		92.7d	96.5d	90.2d				89.5d	90.7d
C-2		64.6d	65.6d	60.6d					72.5d, 70.3d,
C-3–C-5		73.8d	78.0d	70.8d					69.8d, 68.4d,
		73.5d	75.6d	70.0d					68.2d, 68.1d,
		71.9d	72.1d	67.5d					67.2d, 64.3d
C-6		62.7t	62.8t	61.3t				61.2t	61.8t
C-1′		150.2d	150.2d	144.2d				146.0d	148.1d
C-2′		110.5d	110.5d	112.1d				114.7d	113.8d
AcO				170.5s, 169.9s,					170.5s, 170.5s,
				169.5s, 168.6s					169.8s, 169.5s,
				20.7q, 20.6q,					168.7s,
				20.5q					20.8q, 20.7q, 20.5q,
									20.5q

[a] In $CDCl_3$; ^{1}H- and ^{13}C-n.m.r. data at 200 and 50.3 MHz, respectively, unless otherwise indicated. [b] ^{1}H-n.m.r. spectrum at 60 MHz; D_2O for ^{1}H, CD_3OD for ^{13}C. [c] In CD_3OD.

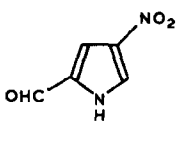
the crystalline tetra-acetates **13** and **15**. Periodate oxidation of **12** afforded known[16] 4-nitro-2-pyrrolecarbaldehyde (**16**). The transformation of **6** into **12**, which could be monitored by ^{1}H-n.m.r. spectroscopy, demonstrated the intermediacy of the sugar nitroenamines **6** and **8** in the formation of the pyrroles **12** and **14**.

The reactions of 1-amino-1-deoxy-D-fructose and its *N*-methyl, *N*-butyl, and *N*-*p*-tolyl derivatives with ENE in methanol at 0° gave chromatographically almost pure products, the instability of which precluded their further purification. Their acetylation afforded mixtures (t.l.c.) of acetates. These products were, most likely, the *N*-(2-nitrovinyl) derivatives of the amino ketoses, which, similarly to the related *N*-(2,2-diacylvinyl) derivatives[17], exist as complex mixtures of isomeric forms differing in the ring size and the anomeric configuration. When these crude products were heated in methanol, or when the reactions of the 1-amino-1-deoxy-D-fructoses with ENE were performed in refluxing methanol or acetone–water, the nitropyrroles **17, 19, 21**, and **23** were obtained (20–60% yields). Their acetylation afforded the corresponding tetra-acetates **18, 20, 22**, and **24**; with the exception of **17**, all of these compounds were crystalline. The periodate oxidations of **17, 19, 21**, and **23** gave the anticipated 4-nitro-3-pyrrolecarbaldehydes **25–28**.

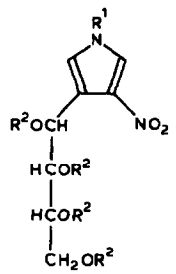
The i.r. (see Experimental) and n.m.r. spectra (Table III) of the 2- and 3-(alditol-1-yl)-4-nitropyrroles **12–15** and **18–24** were consistent with the proposed structures. It is interesting to note that the acetylated 4-(alditol-1-yl)-3-nitropyrroles **18, 20, 22**, and **24** had $J_{1',2'}$ (2.7–2.9 Hz) and $J_{2',3'}$ (8.6–8.8 Hz) values which indicated that C-4 and the alditolyl carbon chain adopt, in solution, a nearly planar zigzag conformation (**29**⇌**30**). On the other hand, the $J_{1',2'}$ (~4.0 Hz) and $J_{2',3'}$ (7.7 Hz) values for the compounds with the alditolyl chain at position 5 suggested contributions of several rotameric states around the C-1′–C-2′ and C-2′–



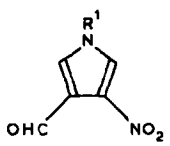
12 $R^1 = R^2 = H$
13 $R^1 = H, R^2 = Ac$
14 $R^1 = Bu, R^2 = H$
15 $R^1 = Bu, R^2 = Ac$



16



17 $R^1 = R^2 = H$
18 $R^1 = H, R^2 = Ac$
19 $R^1 = Me, R^2 = H$
20 $R^1 = Me, R^2 = Ac$
21 $R^1 = Bu, R^2 = H$
22 $R^1 = Bu, R^2 = Ac$
23 $R^1 = p\text{-}Me\text{-}C_6H_4, R^2 = H$
24 $R^1 = p\text{-}Me\text{-}C_6H_4, R^2 = Ac$



25 $R^1 = H$
26 $R^1 = Me$
27 $R^1 = Bu$
28 $R^1 = p\text{-}Me\text{-}C_6H_4$

TABLE III

N.M.R. DATA[a] (δ, p.p.m.; J, Hz) FOR **12**, **13**, **15**, AND **18**–**24**

Nucleus	*Compounds*									
	12[b]	**13**[c]	**15**	**18**	**19**[d]	**20**	**21**[d]	**22**	**23**[e]	**24**
NH		10.0br		8.95br						
H-2				6.68ddd $J_{2,5}$ 2.5 $J_{2,1'}$ 0.6 $J_{NH,2}$ 2.0	6.80dd $J_{2,5}$ 2.7 $J_{2,1'}$ 0.7	6.58dd $J_{2,5}$ 2.8 $J_{2,1'}$ 0.8	6.86dd $J_{2,5}$ 2.7 $J_{2,1'}$ 0.7	6.61dd $J_{2,5}$ 2.7 $J_{2,1'}$ 0.7	7.34dd $J_{2,5}$ 2.7 $J_{2,1'}$ 1	6.92dd $J_{2,5}$ 2.8 $J_{2,1'}$ 0.7
H-3	6.65dd $J_{3,5}$ 1.8 $J_{3,1'}$ 0.6	6.77m $J_{3,5}$ 1.8	6.71d $J_{3,5}$ 2.0							
H-5	7.67d	7.64m	7.48d	7.61dd $J_{NH,5}$ 3.5	7.83d	7.46d	7.90d	7.94d	8.36d	7.85d
H-1′	4.97d,br $J_{1',2'}$ 1.4	6.04d $J_{1',2'}$ 5.3	6.04d $J_{1',2'}$ 4.0	6.63dd $J_{1',2'}$ 2.9	5.31ddd $J_{1',2'}$ 1.9 $J_{OH,1'}$ 6.2	6.50dd $J_{1',2'}$ 2.8	5.32dd $J_{1',2'}$ 1.4	6.52dd $J_{1',2'}$ 2.7	5.38ddd $J_{1',2'}$ 1.6 $J_{OH,1'}$ 6.8	6.69dd $J_{1',2'}$ 2.8
H-2′		5.58t $J_{2',3'}$ 6	5.40dd $J_{2',3'}$ 7.7	5.66dd $J_{2',3'}$ 8.7	3.3–3.6m	5.65dd $J_{2',3'}$ 8.6	3.3–3.7m	5.66dd $J_{2',3'}$ 8.8	3.3–3.7m	5.72dd $J_{2',3'}$ 8.7
H-3′		5.15m	5.23ddd $J_{3',4'a}$ 2.7 $J_{3',4'b}$ 5.2	5.29ddd $J_{3',4'a}$ 2.6 $J_{3',4'b}$ 5.2	3.3–3.6m	5.28ddd $J_{3',4'a}$ 2.7 $J_{3',4'b}$ 5.2	3.3–3.7m	5.28ddd $J_{3',4'a}$ 2.7 $J_{3',4'b}$ 5.0	3.3–3.7m	5.33ddd $J_{3',4'a}$ 2.6 $J_{3',4'b}$ 5.0
H-4′a		4.35–4.11m	4.28dd $J_{4'a,4'b}$ 12.6	4.30dd $J_{4'a,4'b}$ 12.4	3.3–3.6m	4.29dd $J_{4'a,4'b}$ 12.4	3.3–3.7m	4.28dd $J_{4'a,4'b}$ 12.4	3.3–3.7m	4.32dd $J_{4'a,4'b}$ 12.4
H-4′b		4.35–4.11m	4.14dd	4.17dd	3.3–3.6m	4.16dd	3.3–3.7m	4.18dd	3.3–3.7m	4.20dd
OAc		2.09s 2.05s	2.11s 2.08s 2.06s 2.05s	2.13s 2.12s 2.04s 1.95s		2.12s 2.12s 2.05s 1.97s		2.13s 2.12s 2.05s 1.94s		2.14s 2.14s 2.06s 1.97s
C-2		132.6s	128.1s	116.5d	124.1d	121.3d	122.4d	120.0d	120.0d	119.2d
C-3		107.5d	105.7d	117.9s	123.6s	116.8s	124.3s	116.9s	124.7s	117.9s
C-4		138.4s	136.2s	134.6s	133.2s	133.4s	132.7s	133.6s	134.6s	135.2s
C-5		121.1d	122.4d	121.2d	125.9d	124.1d	124.1d	123.1d	121.0d	121.6d
C-1′		67.0d	64.7d	67.9d	65.9d	66.5d	65.2d	66.7d	64.8d	66.6d
C-2′		68.6d	69.8d	69.9d	73.6d	69.6d	73.2d	69.8d	72.6d	69.7d
C-3′		68.6d	69.1d	68.6d	72.4d	68.3d	72.0d	68.4d	71.5d	68.4d
C-4′		62.2t	61.8t	62.2t	64.3t	62.0t	63.7t	62.2t	63.6t	62.1t
AcO		170.0s	170.5s	170.9s		170.6s		170.8s		170.7s
		169.9s	169.8s	170.3s		170.0s		170.2s		170.2s
		169.6s	169.7s	169.7s		169.5s		169.5s		169.5s
		169.5s	169.3s	169.3s		169.0s		168.9s		169.0s
		20.8q	20.7q	20.8q		20.7q		20.9q		20.8q
		20.7q	20.7q	20.8q		20.6q		20.8q		20.8q
		20.6q	20.6q	20.7q		20.6q		20.7q		20.7q
		20.5q	20.6q	20.7q		20.3q		20.5q		20.5q

[a] In $CDCl_3$; ^{1}H- and ^{13}C-n.m.r. spectral data at 200 and 50.3 MHz, respectively, unless otherwise indicated. [b] In CD_3OD. [c] ^{1}H-N.m.r. spectrum at 60 MHz. [d] In $(CD_3)_2SO$.

TABLE IV

N.M.R. SPECTRAL DATA[a] (δ, p.p.m.; J, Hz) FOR COMPOUNDS **16** AND **25–28**

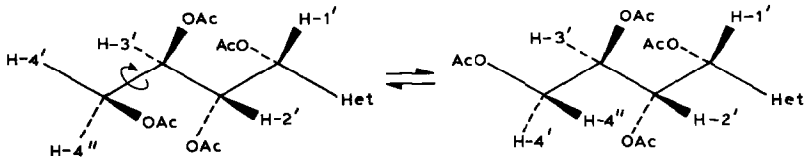
Nucleus	**16**	**25**	**26**	**27**	**28**
NH	10.34br	10.5br			
H-2		7.46m	7.28d	7.31d	7.65d
		$J_{2,5}$ 2.2[b]	$J_{2,5}$ 2.6	$J_{2,5}$ 2.7	$J_{2,5}$ 2.6
H-3	7.93m				
	$J_{3,5}$ 1.6[b]				
H-5	7.51s,br	7.68m	7.52d	7.53d	7.89d
CHO	9.63t	10.44s	10.39s	10.40s	10.47s
	$J_{3,CHO}$ 1.1[b]				
C-2	104.1s		124.5d	123.5d	120.6d
C-3	114.6d		120.1s	[c]	124.4s
C-4	131.4s		135.5s	[c]	[c]
C-5	124.7d		126.5d	125.5d	122.4d
CHO	180.1d		185.7d	185.9d	185.8d

[a]In $CDCl_3$; ^1H- and ^{13}C-n.m.r. spectral data at 200 and 50.3 MHz, respectively. [b]Measured in the *N*-deuterated derivative. [c]Not located.

C-3′ bonds. The n.m.r. spectral data (Table IV) for the 4-nitro-2- and -3-pyrrolecarbaldehydes were also consistent with the assigned structures. The $J_{3,5}$ and $J_{3,CHO}$ values for **16** were measured after deuteration of the sample; the signals of H-5 and the aldehyde proton then appeared as doublets ($J_{3,5}$ 1.6, $J_{3,CHO}$ 1.1 Hz, respectively), and H-3 gave a broad triplet (coupling to H-5 and CHO). A similar experiment with the *N*-deuterated derivative **25** gave a $J_{2,5}$ value of 2.2 Hz; no coupling was observed between the CHO proton and H-2.

EXPERIMENTAL

General. — Melting points were determined in open glass capillaries in a Buchi apparatus and are uncorrected. Optical rotations were recorded with a Perkin–Elmer 241 Mc polarimeter. I.r. spectra were recorded with a Perkin–Elmer 299 spectrophotometer. ^1H- and ^{13}C-n.m.r. spectra were determined at 200 and 50 MHz, respectively, with a Varian XL-200 spectrometer, unless otherwise indicated; chemical shifts refer to internal Me_4Si. *N*-Deuteration of the pyrroles for ^1H-n.m.r.



spectroscopy was performed by shaking a solution of the sample in $CDCl_3$ with a few drops of D_2O. Assignments of the ^{13}C-n.m.r. spectra of the pyrroles **18**, **20**, **22**, and **24** were confirmed by heteronuclear decoupling experiments. T.l.c. was performed on Silica Gel $60F_{254}$ (Merck) with detection with u.v. light (254 nm) and/or by charring with sulfuric acid. Column chromatography was performed with Silica Gel 60 (230–400 mesh; Merck). Elemental analyses were conducted at the Instituto de Química Orgánica General, C.S.I.C., Madrid. Solutions were dried with $MgSO_4$ and concentrated under diminished pressure at <50°. Acetates were prepared by treating a cooled solution of the polyol (1 part) in pyridine (10 parts) with acetic anhydride (5 parts); after 24 h at 0°, the mixture was poured onto ice, and the crystalline precipitate (unless otherwise stated) was recrystallised from the solvent indicated.

*2-Deoxy-2-[(2-nitrovinyl)amino]-α,β-*D*-glucopyranose* (**6**) *and its 1,3,4,6-tetra-acetate* (**7**). — A solution of 2-amino-2-deoxy-β-D-glucopyranose (0.72 g, 4 mmol) in H_2O (5 mL) was treated with ENE[18] (0.47 g, 4 mmol), acetone was added to obtain a homogeneous solution, and the mixture was stored at 0° for 2 h. T.l.c. ($CHCl_2$–MeOH, 10:1) then indicated the quantitative formation of **6**. The acetone was evaporated, and the aqueous solution was extracted with benzene and then freeze-dried. The amorphous product (1 g, ~100%) was chromatographically pure **6**, but was unstable and darkened on storage. The i.r. and n.m.r. data for freshly prepared samples are recorded in Tables I and II, respectively.

Acetylation of **6** afforded 83% of a ~4:1 mixture (^1H-n.m.r. data) of **7α** + **7β**, m.p. 140–142° (from EtOH).

Anal. Calc. for $C_{16}H_{22}N_2O_{11}$: C, 45.9; H, 5.3; N, 6.7. Found: C, 46.3; H, 5.4; N, 6.9.

Column chromatography (ether–hexane) of **7α** + **7β** afforded **7α**, m.p. 143–144° (from EtOH), $[\alpha]_D^{26}$ +174° (*c* 1.2, chloroform). The i.r. and n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{16}H_{22}N_2O_{11}$: C, 45.9; H, 5.3; N, 6.7. Found: C, 46.0; H, 5.1; N, 6.8.

*2-[N-Butyl-(2-nitrovinyl)amino]-2-deoxy-α,β-*D*-glucopyranose* (**8**) *and its 1,3,4,6-tetra-acetate* (**9**). — ENE (0.35 g, 3 mmol) was added to a stirred suspension of 2-butylamino-2-deoxy-α,β-D-glucopyranose[19] (0.50 g, 2.13 mmol) in MeOH (15 mL). The sugar dissolved rapidly, and the solution was stored at 0° for 2 h. Concentration left a foamy residue which was extracted with C_6H_6. The product (0.65 g, ~100%), which was chromatographically homogeneous, decomposed on storage. The spectral data of freshly prepared samples are given in Tables I and II.

Acetylation gave a syrupy product, column chromatography of which (Et_2O–hexane, 1:1) afforded **9** (0.86 g, 85%), m.p. 65–66° (from Et_2O–hexane). I.r. and n.m.r. data are given in Tables I and II.

Anal. Calc. for $C_{20}H_{30}N_2O_{11}$: C, 50.6; H, 6.4; N, 5.9. Found: C, 50.8; H, 6.4; N, 6.3.

*1-(β-*D*-Glucopyranosylamino)-2-nitroethene* (**10**) *and its 2',3',4',6'-tetra-*

acetate (**11**). — A suspension of β-D-glucopyranosylamine (0.90 g, 5 mmol) in MeOH (10 mL) containing ENE (0.59 g, 5 mmol) was stirred vigorously at room temperature until all the sugar had dissolved (~50 h). Concentration of the resulting solution afforded **10** as a chromatographically (t.l.c.) homogeneous syrup which was acetylated. Column chromatography (Et_2O) of the resulting syrupy material afforded **11** (26%), m.p. 186–187° (from EtOH), $[\alpha]_{5461}^{26}$ +19° (*c* 1, chloroform). I.r. data are given in Table I. N.m.r. data ($CDCl_3$): ^1H (60 MHz), δ 2.01 (s, 3 H, AcO), 2.02 (s, 6 H, AcO), 2.07 (s, 3 H, AcO), 4.0–4.3 (m, 3 H, H-5′,6′,6′), 4.6–5.3 (m, 4 H, H-1′,2′,3′,4′), 6.49 (d, $J_{1,2}$ 6.3, H-2), 6.73 (dd, $J_{NH,1}$ 13.0, H-1), 8.89 (dd, $J_{NH,1'}$ 8.2, NH); ^{13}C (50.3 MHz), δ 20.5 (q, CH_3CO), 20.6 (q, CH_3CO), 20.7 (q, CH_3CO), 62.1 (t, C-6′), 68.6 (d, C-4′), 71.0 (d, C-2′), 72.5 (d, C-3′), 72.9 (d, C-5′), 87.4 (d, C-1′), 113.6 (d, C-2), 142.3 (d, C-1), 169.5 (s, CO_2), 170.1 (s, CO_2), 170.6 (s, CO_2), 170.7 (s, CO_2).

Anal. Calc. for $C_{16}H_{22}N_2O_{11}$: C, 45.9; H, 5.3; N, 6.7. Found: C, 46.0; H, 5.3; N, 6.7.

*4-Nitro-2-(*D-arabino-*tetritol-1-yl)pyrrole* (**12**) *and its 1′,2′,3′,4′-tetra-acetate* (**13**). — (*a*) To a stirred solution of 2-amino-2-deoxy-D-glucose hydrochloride (1 g, 4.64 mmol) and Na_2CO_3 (0.25 g, 2.32 mmol) in H_2O (3–4 mL) were added ENE (0.54 g, 4.64 mmol) and the acetone required to obtain a homogeneous solution. The mixture was heated under reflux for 8–10 h, the acetone was evaporated, and the aqueous solution was extracted with benzene and then freeze-dried. The foamy residue contained **12** (t.l.c., CH_2Cl_2–MeOH, 3:1) as the main product. Its ^1H-n.m.r. data are given in Table III.

Acetylation of the above mixture and column chromatography (Et_2O–hexane) of the syrupy product afforded the tetra-acetate **13** (0.44 g, 24%), m.p. 160–162° (from Et_2O–hexane), $[\alpha]_D^{27}$ −33° (*c* 1, chloroform); ν_{max}^{KBr} 3460w (NH), 1738s (AcO), 1536m and 1504m cm^{-1} (NO_2). The n.m.r. data are given in Table III.

Anal. Calc. for $C_{16}H_{20}N_2O_{10}$: C, 40.0; H, 5.0; N, 7.0. Found: C, 40.2; H, 4.8; N, 6.8.

(*b*) A solution of **6** (200 mg) in CD_3OD (1 mL) was heated at 50°. The reaction was monitored by ^1H-n.m.r. spectroscopy (loss of the signals of H-1′ and H-2′ of **6**, and the appearance of the signals of H-3 and H-5 of **12**). After 8 h, the spectrum corresponded to that of **12**, with low-intensity signals due to by-products.

*1-Butyl-4-nitro-2-(*D-arabino-*tetritol-1-yl)pyrrole* (**14**) *and its 1′,2′,3′,4′-tetra-acetate* (**15**). — Treatment of 2-butylamino-2-deoxy-α,β-D-glucopyranose[19] with ENE, as described above for the preparation of **12**, afforded **14** as a syrup, which gave the tetra-acetate **15** (25%), m.p. 97–98° (from Et_2O–hexane), $[\alpha]_D^{27}$ −24° (*c* 1, chloroform); ν_{max}^{KBr} 1740s (AcO), 1512s (NO_2), and 1502s,sh cm^{-1}. The n.m.r. data are given in Table III.

Anal. Calc. for $C_{20}H_{28}N_2O_{10}$: C, 52.6; H, 6.2; N, 6.1. Found: C, 52.5; H, 6.2; N, 6.2.

4-Nitro-2-pyrrolecarbaldehyde (**16**). — A solution of **12** (232 mg, 1 mmol) in H_2O (30 mL) was stirred with $NaIO_4$ (910 mg, 3 mmol) and Et_2O (30 mL). After 40 h, the mixture was extracted with Et_2O, and the extract concentrated. Column chromatography (Et_2O–hexane) of the syrupy residue afforded **16** (28%), m.p. 136–137° (from Et_2O–hexane; lit.[16], m.p. 142°); ν_{max}^{KBr} 3235m (NH), 1664s (C=O), 1558m, and 1510s cm^{-1} (NO_2). The n.m.r. data given in Table IV.

*4-Nitro-3-(*D-arabino-*tetritol-1-yl)pyrrole* (**17**) *and its 1',2',3',4'-tetra-acetate* (**18**). — To a solution of 1-amino-1-deoxy-D-fructose acetate[20] (0.96 g, 4 mmol) and Na_2CO_3 (0.42 g, 4 mmol) in H_2O (5 mL) were added ENE (0.47 g, 4 mmol) and the amount of acetone required to obtain a homogeneous solution. Work-up of the reaction mixture, as indicated for **12**, gave a foam, acetylation of which gave, after column chromatography, the tetra-acetate **18** (18%), m.p. 120–122° (from Et_2O–hexane), $[\alpha]_D^{33}$ +3° (*c* 1, chloroform); ν_{max}^{KBr} 3465w (NH), 1742s (AcO), and 1504s cm^{-1} (NO_2). The n.m.r. data are given in Table III.

Anal. Calc. for $C_{16}H_{20}N_2O_{10}$: C, 40.0; H, 5.0; N, 7.0. Found: C, 39.7; H, 5.3; N, 6.8.

*1-Methyl-4-nitro-3-(*D-arabino-*tetritol-1-yl)pyrrole* (**19**) *and its 1',2',3',4'-tetra-acetate* (**20**). — Treatment of 1-deoxy-1-methylamino-D-fructose acetate[21] with ENE, as described for **17**, gave **19** (57%), m.p. 195–196° (from H_2O), $[\alpha]_D^{33}$ −137° (*c* 1, pyridine); ν_{max}^{KBr} 1518s cm^{-1} (NO_2).

Anal. Calc. for $C_9H_{14}N_2O_5$: C, 43.9; H, 5.7; N, 11.4. Found: C, 43.5; H, 5.6; N, 11.3.

The tetra-acetate **20** (75%) had m.p. 168–169° (from EtOH), $[\alpha]_D^{33}$ +7° (*c* 1, chloroform); ν_{max}^{KBr} 1740s (AcO) and 1522s cm^{-1} (NO_2).

Anal. Calc. for $C_{17}H_{22}N_2O_{10}$: C, 49.3; H, 5.4; N, 6.8. Found: C, 49.0; H, 5.4; N, 6.7.

*1-Butyl-4-nitro-3-(*D-arabino-*tetritol-1-yl)pyrrole* (**21**) *and its 1',2',3',4'-tetra-acetate* (**22**). — Treatment of 1-butylamino-1-deoxy-D-*arabino*-hexulose oxalate[22] with ENE, as described for **17**, gave **21** (42%), m.p. 133–134° (from EtOH), $[\alpha]_D^{33}$ −75° (*c* 1, pyridine); ν_{max}^{KBr} 1518 cm^{-1} (NO_2).

Anal. Calc. for $C_{12}H_{20}N_2O_6$: C, 50.0; H, 7.0; N, 9.7. Found: C, 49.9; H, 7.1; N, 9.7.

The tetra-acetate **22** (86%) had m.p.97–98° (from EtOH), $[\alpha]_D^{33}$ −5° (*c* 1, chloroform); ν_{max}^{KBr} 1738s (AcO) and 1512m cm^{-1} (NO_2).

Anal. Calc. for $C_{20}H_{28}N_2O_{10}$: C, 52.6; H, 6.2; N, 6.1. Found: C, 52.6; H, 6.2; N, 5.9.

The n.m.r. data for **21** and **22** are given in Table III.

*4-Nitro-3-(*D-arabino-*tetritol-1-yl)-1-*p*-tolylpyrrole* (**23**) *and its 1',2',3',4'-tetra-acetate* (**24**). — To a hot solution of 1-deoxy-1-*p*-tolylamino-D-*arabino*-hexulose[23] (1.35 g, 5 mmol) in MeOH (15 mL) were added ENE (0.59 g, 5 mmol) and triethylamine (0.7 mL, 5 mmol), and the mixture was heated for 36 h. Evaporation of the solvent afforded **23** (15%), m.p. 205–206° (from MeOH), $[\alpha]_D^{33}$ −24° (*c* 1, pyridine); ν_{max}^{KBr} 1522s cm^{-1} (NO_2).

Anal. Calc. for $C_{15}H_{18}N_2O_6$: C, 56.3; H, 5.3; N, 5.7. Found: C, 56.6; H, 5.3; N, 5.7.

The tetra-acetate **24** (84%) had m.p. 151–152° (from EtOH), $[\alpha]_D^{33}$ −11° (*c* 1, chloroform); ν_{max}^{KBr} 1740s (AcO) and 1520s cm^{-1} (NO_2).

Anal. Calc. for $C_{23}H_{26}N_2O_{10}$: C, 56.3; H, 5.3; N, 5.7. Found: C, 56.6; H, 5.3; N, 5.7.

The n.m.r. data for **23** and **24** are given in Table III.

4-Nitro-3-pyrrolecarbaldehyde (**25**). — To a stirred solution of **17** (0.20 g, 0.71 mmol) in H_2O (20 mL) were added $NaIO_4$ (0.46 g, 2.1 mmol) and Et_2O. After stirring for 4 h, the ether layer was separated and the aqueous layer was extracted twice with Et_2O. The combined ether extracts were dried and concentrated. Column chromatography (Et_2O–hexane) of the residue gave **25** (8%), m.p. 184–186° (from EtOH; lit.[16], m.p. 189°). The n.m.r. data are given in Table IV.

1-Methyl-4-nitro-3-pyrrolecarbaldehyde (**26**). — A suspension of **19** (0.25 g, 1 mmol) in H_2O (30 mL), covered with a layer of Et_2O (30 mL), was treated with $NaIO_4$ (1.1 g, 3 mmol), and the mixture was stirred for 4 h. The ether layer was separated, and the aqueous layer was extracted with Et_2O. Concentration of the combined ether extracts gave **26** (0.10 g, 66%), m.p. 167–168° (from EtOH); ν_{max}^{KBr} 1666s (C=O) and 1525m cm^{-1} (NO_2). The n.m.r. spectral data are given in Table IV.

Anal. Calc. for $C_6H_6N_2O_3$: C, 46.8; H, 3.9; N, 18.2. Found: C, 46.6; H, 3.8; N, 18.1.

1-Butyl-4-nitro-3-pyrrolecarbaldehyde (**27**). — Compound **27**, prepared (38%) from **21** as described for **26**, had m.p. 61–63° (from EtOH); ν_{max}^{KBr} 1671s (C=O) and 1526 cm^{-1} (NO_2). The n.m.r. data are given in Table IV.

Anal. Calc. for $C_9H_{12}N_2O_3$: C, 55.1; H, 6.2; N, 14.3. Found: C, 54.8; H, 6.2; N, 14.2.

*4-Nitro-1-*p*-tolylpyrrole-3-carbaldehyde* (**28**). — Compound **28**, prepared (84%) from **24** as described for **26**, had m.p. 129–130° (from EtOH); ν_{max}^{KBr} 1672s (C=O) and 1526s cm^{-1} (NO_2). The n.m.r. data are given in Table IV.

Anal. Calc. for $C_{12}H_{10}N_2O_3$: C, 62.6; H, 4.4; N, 12.2. Found: C, 62.4; H, 4.6; N, 12.1.

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