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N.M.R. STUDIES OF D-RIBOSYLAMINES IN SOLUTION: DERIVATIVES OF PRIMARY AMINES*

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ABSTRACT

N.m.r. spectroscopy (^1H, ^{13}C) has been used to show that primary amines condense with D-ribose to give mainly D-ribopyranosylamines in which the α anomer in the $^1C_4$ conformation preponderates; the β anomer assumes mainly the $^4C_1$ conformation. Thus, it is possible to deduce the structures of the *N*-phenyl-D-ribosylamines and to correlate some of the literature data. For 2,3-*O*-isopropylidene-D-ribofuranosylamine derivatives, the $\Delta\delta$ values for the ^{13}C-n.m.r. signals of the isopropylidene methyl groups can be used to establish the anomeric configuration.

INTRODUCTION

Glycosylamines are a long-known[1] and widely exemplified class of carbohydrate derivative, some of which (nucleosides, glycopeptides) are of exceptional biological interest; others are valuable synthetic intermediates in nucleoside chemistry[2]. Moreover, in some cases, the glycosyl moiety can be considered as a biological carrier[3] and used in the pro-drug approach.

Among the main preparative procedures[4] for glycosylamines, the reaction between a sugar and the appropriate amine with an alcohol as the solvent, and with or without an acid catalyst, is the simplest. Such methods as condensation between amines and acylglycosyl halides, transglycosylation reactions, or reduction of Schiff's bases can be classed as indirect procedures. The stability of glycosylamines[5] is strongly dependent on the basicity of the aglycon, the hybridisation state and degree of substitution of the nitrogen atom, the structure of the sugar moiety, and the pH of the solution.

Glycosylamines exhibit mutarotation phenomena and can rearrange into isomeric compounds. Crystallisation, when possible, often occurs with one or several molecules of water, alcohol, or amine. These properties often complicate the isolation and structural determination of glycosylamines; in the latter context, ^1H- and ^{13}C-n.m.r. spectroscopy are the most appropriate methods.

*Part I.

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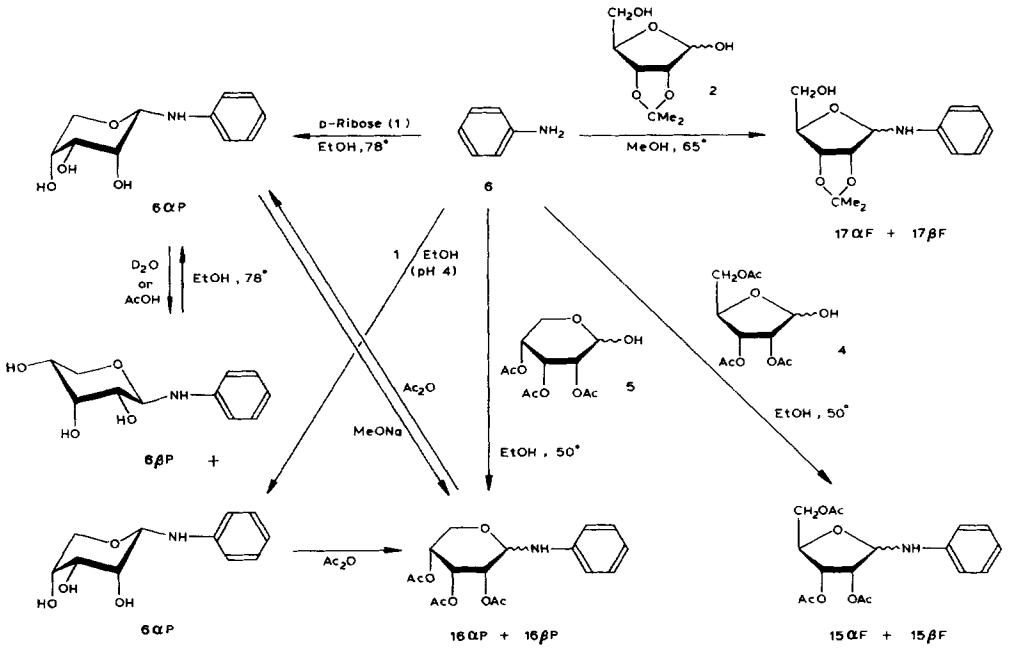
We now report a general study of the products of the direct condensation of primary aliphatic or aromatic amines and D-ribose.

Ribosylamine[6] is an intermediate in the preparation of pyrimidine and imidazole nucleosides, phenylethylamine and tryptamine are present in living organisms and their glucosyl derivatives are known[7], **13** (as many steroidal amines[8]) is active on the central nervous system, and **14** is an intermediate in the biosynthesis of purine nucleotides[9].

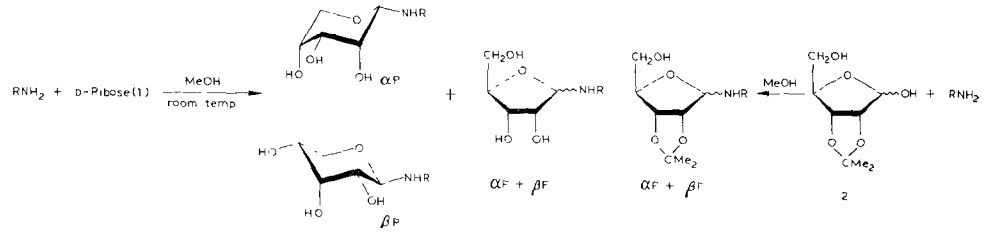
RESULTS AND DISCUSSION

The following amines were investigated: aniline (**6**), ammonia (**7**), benzylamine (**8**), phenylethylamine (**9**), tryptamine (**10**), 2,2-diethoxyethylamine (**11**), cyclohexylamine (**12**), 17β-amino-3β-hydroxyandrost-5-ene (**13**), and 5-amino-4-carbamoylimidazole (**14**).

Each of these amines was condensed with D-ribose (**1**), with an alcohol as solvent (Schemes 1 and 2) at room temperature in order to avoid the Maillard degradation reaction[10]. The time necessary for completion of reaction ranged from a few to 24 h. Acyclic, furanoid, and pyranoid products are possible. Reference furanoid compounds were obtained by the reaction of **6–14** (Scheme 2) with 2,3-*O*-isopropylidene-D-ribofuranose (**2**), since the presence of a five-membered ring strongly favors the formation of a second, fused, five-membered ring[11]. In these condensations with



Scheme 1



Amine	Compounds	Compounds
Ammonia (7)	7αP + 7βP + 7αF + 7βF	18αF + 18βF
Benzylamine (8)	8αP + 8βP + 8αF + 8βF	19αF + 19βF
Phenylethylamine (9)	9αP + 9βP + 9αF + 9βF	20αF + 20βF
Tryptamine (10)	10αP + 10βP + 10αF + 10βF	21αF + 21βF
2,2-Diethoxyethylamine (11)	11αP + 11βP + 11αF + 11βF	22αF + 22βF
Cyclohexylamine (12)	12αP + 12βP + 12αF + 12βF	23αF + 23βF
17β-Amino-3β-hydroxyandrost-5-ene (13)	13αP + 13βP + 13αF + 13βF	24αF + 24βF
5-Amino-4-carbamoylimidazole (14)	14αP + 14βP + 14αF + 14βF	25αF + 25βF

Scheme 2

2, the reaction times at room temperature were much greater than those for **1**, because of the lower reactivity of **2**. The reactions could be carried out at reflux temperature in anhydrous methanol, since Maillard or Amadori[12] side-reactions are precluded. Usually, the D-ribosylamine derivatives were obtained crystalline directly, but those from **7** and **9** required chromatography before crystallisation.

N.m.r. spectroscopy was performed on solutions in such polar solvents as pyridine-d_5 or Me_2SO-d_6, which are known to influence the equilibrium between the different isomers and their conformers by way of complex formation[9] and suppression[13] of intramolecular hydrogen-bonding.

In the following discussion, the terms αP, βP, αF, and βF connote α-pyranose, β-pyranose, α-furanose, and β-furanose, respectively.

*N-Phenyl-*D*-ribosylamines*

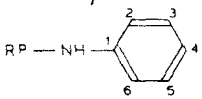
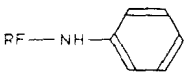
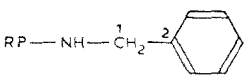
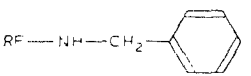
When this manuscript was being prepared, some data were reported[14] on the identification of two crystalline *N*-phenyl-D-ribosylamines using ^{13}C- and ^{1}H-n.m.r. spectroscopy. Our findings are similar, and hence our results with aniline will be noted only briefly.

The ^{13}C-n.m.r. spectrum of the condensation product of aniline with 2,3-*O*-isopropylidene-D-ribofuranose (Scheme 1) showed the presence of the two anomeric compounds **17**αF and **17**βF (Table II).

The reaction[15a] of D-ribose (**1**) and aniline (**6**) in ethanol at pH 4 (Scheme 1) afforded 92% of a product that had m.p. 125–126°, $[\alpha]_D^{20}$ +60° (*c* 1, pyridine); lit.[15a] m.p. 125–127°, $[\alpha]_D^{20}$ +63.4° (*c* 1, pyridine). The ^{13}C-n.m.r. spectrum of this material revealed the presence of **6**αP and **6**βP in nearly equal proportions. However, the ^{13}C-n.m.r. spectrum of the crude product before recrystallisation contained (Table I) four signals for anomeric carbons. The pair of signals at high field are assigned to **6**αF and **6**βF by comparison with those for **17**αF and **17**βF,

TABLE I

^{13}C-N.M.R. DATA[a] FOR D-RIBOSYLAMINE DERIVATIVES

R-X[b]		%	*C-1*	*1C-1*	*C-2*	*C-3*	*C-4*	*C-5*	C_{base}			
RP—OH	β	60	94.50	0.78	71.91	68.49	67.94	63.24				
1αP + 1βP	α	30	93.72		70.68	69.31	67.16	60.50				
RF—OH	β	6	101.52	5.34	75.61	71.04	83.23	63.01				
1αF + 1βF	α	4	96.18		70.81	70.27	82.95	61.73				
									*C-1*	*C-3,5*	*C-4*	*C-2,6*
RP—NH—	β	50	81.59	0.34	70.42	70.08	67.40	63.08	147.13	128.70	116.90	113.05
6αP + 6βP	γ	35	81.25		69.93	69.93	67.84	62.09	146.16	128.70	117.19	113.29
												
RF—NH—	β	10	87.88	4.15	73.88	70.03	83.05	62.09				
6αF + 6βF	α	5	83.73		71.43	n.d.[c]	81.54	61.25				
RP—NH_2	β	40	83.44	1.07	72.13	71.98	67.50	66.08				
7αP + 7βP	α	50	82.37		70.03	69.20	68.47	63.64				
RF—NH_2	β	7	89.88	4.00	75.40	70.62	82.37	62.23				
7αF + 7βF	α	3	85.88		70.76	n.d.	80.92	61.79				
									*C-1*		*C-2*	*Ph*
RP—NH—CH_2—	β	50	86.52	0.28	70.86	71.30	67.68	64.86	48.13		140.55	127.87
8αP + 8βP	γ	40	86.24		70.03	69.54	68.52	63.69	48.62			
												
RF—NH—CH_2—	β	7	93.83	4.60	74.18	n.d.	82.81	62.42	48.62		140.74	126.46
8αF + 8βF	α	3	89.23		n.d.	n.d.	81.39	61.83	49.10			

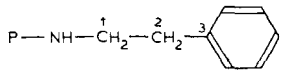
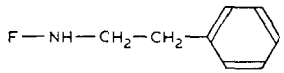
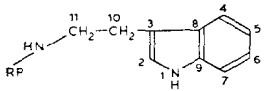
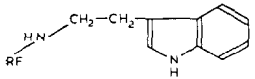
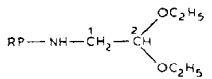
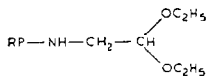
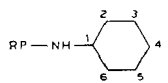
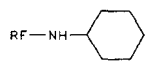
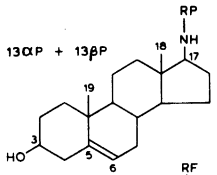
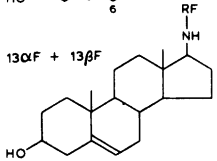
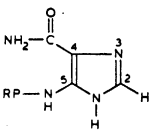
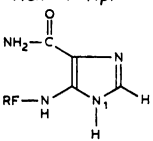
									C-1	*C-2*	*C-3*	*Ph*
	β	40	87.39	0.32	70.77	71.46	67.59	65.13	47.06			125.76
	α	40	87.07		70.00	69.50	68.59	63.67	46.51			128.17
9αP + 9βP										36.37	140.41	128.53
	β	10	94.44	4.14	74.05	71.05	82.70	62.40	47.33			
	α	10	90.30		70.93	70.83	81.33	61.90				
9αF + 9βF												
									C-11	*C-10*	*C-9*	
											136.37	
											C-8	
	β	45	87.57	0.41	70.87	71.59	67.63	65.27	45.20		127.30	
	α	35	87.16		70.14	69.59	68.64	63.77	45.65		*C-2,7*	
											112.65	111.33
10αP + 10βP										26.08	*C-1,6*	
											113.11	118.29
	β	15	94.62	4.09	74.14	70.73	82.84	62.45	46.51		*C-5*	
	α	5	90.53		71.14	n.d.	81.38	61.64			120.79	
10αF + 10βF											*C-2*	
											122.48	
									C-1	*C-2*	*Me*	CH_2
	β	50	87.75	0.54	71.37	70.77	67.63	64.99	47.57	102.41		61.26
	α	30	87.21		70.32	69.77	68.64	63.90	48.11	102.27		61.44
11αP + 11βP											15.34	
	β	12	94.76	4.14	74.10	70.77	82.93	62.45	48.65	103.00		61.63
	α	8	90.62		71.23	70.95	81.61	61.99	48.56			61.85
11αF + 11βF												
									C-1	*C-2,6*	*C-2,5*	
	β	35	84.71	0.39	71.59	70.96	67.59	65.15	52.38	34.43		24.53
	α	45	84.32		69.98	69.54	68.62	63.65	50.82			
12αP + 12βP											25.75	
	β	8	91.78	4.48	74.57	70.52	82.61	61.28	52.77	32.04		24.24
	α	12	87.30		70.96	70.96	81.15	61.72	51.69	32.53		24.09
12αF + 12βF												

TABLE I *(continued)*

R-X[b]		%	*C-1*	*ΔC-1*	*C-2*	*C-3*	*C-4*	*C-5*	C_{base}			
 13αP + 13βP												
	β	42	87.61	1.46	71.20	71.20	67.69	65.75	*C-3*	*C-5*	*C-18*	*C-17*
	α	35	86.15		70.04	70.04	68.37	63.92		141.45	11.45	52.74
 13αF + 13βF									70.04	*C-6*	*C-19*	
	β	15	95.23	5.93	74.65	70.67	82.63	62.51		120.32	11.31	52.97
	α	8	89.30		71.59	70.81	81.58	62.06				
 14αP + 14βP									*C-2*	*C-4*	*C-5*	
	β	72	81.28	0.28	70.77	70.32	67.83	64.56				
	α	23	81.00		70.14	69.59	67.63	63.77				
 14αF + 14βF									130.85	107.85	146.52	164.40
	β	3	87.97	4.09	73.88	n.d.	n.d.	62.41				
	α	2	83.88		n.d.	n.d.	n.d.	61.90				

[a]Chemical shifts (p.p.m.); solutions in $(CD_3)_2SO$ (internal Me_4Si). [b]RP, Ribopyranosyl; RF, ribofuranosyl. [c]Not determined.

and hence the other two signals at lower field represent the preponderant (85%) *N*-phenyl-D-ribopyranosylamines **6**αP and **6**βP (αβ-ratio 1.5:1).

When the condensation between **1** and **6** was carried out in anhydrous methanol at room temperature, the compound obtained (95%) after recrystallisation contained **6**αP and **6**βP in the ratio 4:1.

Following a second literature procedure[15a] (**1** and **6** in boiling, anhydrous ethanol) that was claimed to give a derivative different than for the reaction carried out at pH 4, pure **6**αP was obtained. Treatment of **6**αP with D_2O or 2% of acetic acid in methyl sulfoxide or pyridine-d_5 gave a product mixture similar to that obtained from the reaction at pH 4. Furthermore, when a solution of the mixture of **6**αP and **6**βP in anhydrous ethanol was boiled, **6**αP was regenerated (Scheme 1).

The chemical shifts of the signals for the anomeric protons in **6**αP and **6**βP, together with the $J_{1,2}$ values and the results of decoupling experiments, indicate that **6**βP adopts mainly the $^4C_1$ conformation, and **6**αP mainly the $^1C_4$ conformation. These results are in agreement with those of other workers[14].

In solution in pyridine or methyl sulfoxide, the mutarotation of *N*-phenyl-D-ribosylamines is retarded. Furthermore, from the $[\alpha]_D$ values of **6**αP and of the equimolar mixture of **6**αP and **6**βP, the $[\alpha]_D$ value of **6**βP can be calculated as $\sim -54°$ in pyridine. On this basis, the $[\alpha]_D^{20}$ value of the mixture obtained from the condensation of **6** and **1** in methanol indicates the ratio of **6**αP and **6**βP to be ~4:1, which agrees with the conclusion based on the ^{13}C-n.m.r. data.

Treatment of **6**αP and the mixture of **6**αP and **6**βP with acetic anhydride in anhydrous pyridine afforded the same mixture of **16**αP and **16**βP, as indicated by the ^{13}C-n.m.r. data (see Experimental). Unambiguous syntheses of 2,3,5-tri-*O*-acetyl-*N*-phenyl-D-ribofuranosylamines (**15**) and 2,3,4-tri-*O*-acetyl-*N*-phenyl-D-ribopyranosylamines (**16**) was accomplished (Scheme 1) by condensation of the corresponding sugars **4** and **5** with aniline (**6**) in dry ethanol. Compound **15** was obtained (85% after chromatography) as an equimolar αβ-mixture.

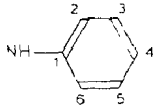
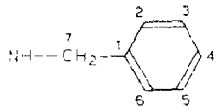
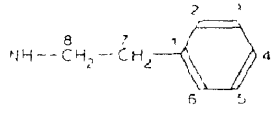
The ^{13}C-n.m.r. spectra (see Experimental) of these compounds were similar to those[5a] of 2,3,5-tri-*O*-benzoyl-*N*-*p*-nitrophenyl-α- and -β-D-ribofuranosylamine obtained by condensation of the appropriate acylglycosyl halide and the amine. The condensation of **5** and **6** gave a mixture of **16**αP and **16**βP (75% after chromatography), with an αβ-ratio of 1:3. A similar mixture was obtained on acetylation of **6**αP or of the mixture of **6**αP and **6**βP. Zemplén deacetylation of the mixture of **16**αP and **16**βP gave only *N*-phenyl-α-D-ribopyranosylamine (**6**αP). Thus, **6**αP appears to be the thermodynamically favoured product of the condensation between aniline and D-ribose.

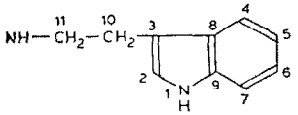
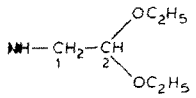
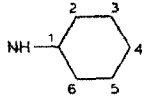
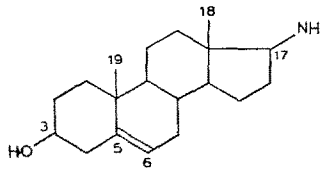
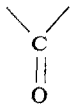
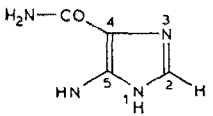
Other D-*ribosylamines*. — As with aniline, the eight other amines were treated first (Scheme 2) with 2,3-*O*-isopropylidene-D-ribofuranose (**2**), in order to obtain authentic furanoid products as reference compounds for ^{13}C-n.m.r. spectroscopy (Table II).

Condensation of D-ribose (**1**) with each of the amines **7**–**14** in methanol yielded a mixture of ribosylamines that gave four ^{13}C resonances (Table I) for anomeric

TABLE II

^{13}C-N.M.R. DATA[a] FOR 2,3-*O*-ISOPROPYLIDENE DERIVATIVES

	X		$^{0}_{0}$	*C-1*	*JC-1*	*C-2*	*C-3*	*C-4*	*C-5*	*O* *C* *O*	*C-Me*	*δC-Me*	*C_{base}*			
2	OH	*β*	100	102.07		86.19	81.95	86.56	62.93	111.24	24.73 26.37	1.64				
													C-1	*C-2,C-6*	*C-3,C-5*	*C-4*
17		*β*	40	90.39	5.46	84.38	81.36	84.11	62.08	112.37	25.08 26.81	1.73	146.37	113.79	128.81	117.65
		α	60	84.93		79.47	81.38	81.56	62.08	111.74	24.94 26.17	1.23	145.92	114.06		117.84
18	NH_2	*β*	45	91.71	4.79	84.73	81.95	86.10	62.51	111.61	24.93 26.78	1.85				
		γ	55	86.92		79.99	81.08	81.80	61.83	110.88	24.87 26.19	1.32				
													C-7	*C-1*	*Ph*	
19		*β*	80	95.15	4.73	85.00	81.64	85.00	62.52	111.19	24.72 26.53	1.81	48.62	139.92	126.51	
		γ	20	90.42		79.49	80.52	81.25	61.69	110.90	24.72 26.14	1.42	49.16	140.50	127.97	
													C-8	*C-7*	*C-1*	*Ph*
20		*β*	60	95.99	4.87	85.02	81.61	84.84	62.54	111.46	24.90 26.67	1.77	46.88	36.05	140.28	125.80 128.17
		γ	40	91.12		79.60	80.92	81.38	61.99	110.92	24.76 26.03	1.27	47.43	36.55	140.18	128.49 128.62

													C-11	*C-10*	*C-3*	*C-7*	
21		β	60	95.83	4.63	84.96	81.54	84.96	62.47	111.34	24.77 26.58	1.81	45.99	25.65	111.34 118.02	112.41	
		α	40	91.20		79.54	80.71	81.40	61.94	110.75	24.77 26.19	1.42	46.72	25.94	*C-5* 120.70 *C-8* 127.14	*C-2* 122.36 *C-9* 136.11	
													C-1	*C-2*			
22		β	55	96.40	5.19	85.07	81.70	84.79	62.63	111.42	24.94 26.67	1.73	48.06	101.91	60.99 61.13	15.25	
		α	45	91.21		79.65	81.02	81.56	61.67	111.01	24.80 26.08	1.28	48.65	102.32	61.31 61.67		
													C-1	*C-2,C-6*	*C-3,C-5*	*C-4*	
23		β	65	93.49	5.02	85.49	81.64	85.05	62.47	111.19	24.72 26.58	1.86	52.28	31.85 34.04		24.24	
		α	35	88.47		79.83	80.81	81.25	61.99	110.75	24.72 26.09	1.37	52.47	32.53 34.67	25.65	24.48	
													C-3		*C-18,19*		
24		β	70	97.05	7.03	85.46	81.86	84.78	62.60	111.29	24.87 26.65	1.78	70.04	52.61	11.45		
		α	30	90.02		79.80	80.62	81.49	61.96	111.10	24.96 26.19	1.23	*C-5* 141.49 *C-6* 120.32	*C-17* 52.97			
													C-2	*C-1*	*C-4*	*C-5*	
25		β	35	90.66	5.96	84.70	81.61	84.25	62.17	112.10	24.99 26.76	1.77	131.49	107.98	107.98	146.54	164.31
		α	65	84.70		78.97	80.92	81.61	61.85	111.78	24.90 26.03	1.13		107.23	107.23	147.15	

[a]Chemical shifts (p.p.m.); solutions in $(CD_3)_2SO$ (internal Me_4Si).

carbons, with those for the pyranoid forms preponderating. The signals for the anomeric carbons of the furanoid derivatives were easily recognised by comparison of their chemical shifts with those of the corresponding signals for the 2,3-*O*-isopropylidene derivatives (Table II).

For the series of $\alpha\beta$-pairs of ribopyranosylamines, the difference in chemical shift for the signal of the anomeric carbons was in the range 0.28–1.07 p.p.m. in Me_2SO-d_6 (except for **12**, for which the difference was 1.46 p.p.m.). From these small values, it may be expected that the pyranoid anomers exist mainly in the $^1C_4$ and $^4C_1$ conformations. This is confirmed by the 100-MHz p.m.r. spectra of the ribopyranosylamines in pyridine-d_5. For each $\alpha\beta$-pair (Table III), after exchange by D_2O, the doublet with $J_{1,2}$ 8 Hz for H-1β was deshielded in comparison with the signal (half-band width 4 Hz) corresponding to H-1α. Suitable irradiation experiments gave partially coupled ^{13}C-p.m.r. spectra in which the signals for the corresponding anomeric carbons were easily recognised. Table IV contains some examples of such decoupled spectra showing that, except for aniline, the rule[15] that C-1α is shielded more than C-1β is not always followed. Thus, there is coalescence of the C-1$\alpha\beta$ peaks for **12**αP and **12**βP or inversion of the predicted positions for **8**αP and **8**βP, and **10**αP and **10**βP. These facts may be explained by conformational inversion, which brings together the anomeric carbon peaks, and this effect may be further amplified by the nitrogen substitution.

The glucosylamines **26** and **27** derived from aniline and β-phenylethylamine were prepared according to the literature[7a,14] (Table V). The anomers of **26** and **27** are known to be in the $^4C_1$ conformation. The signals for H-1 in the *N*-phenylglucosylamines **26**αP and **26**βP were triplets (5.50 and 5.15 p.p.m. in pyridine-d_5) which, after D_2O exchange, afforded a broadened signal ($W_{1/2}$ 4 Hz) for H-1α and

TABLE III

^1H-CHEMICAL SHIFTS FOR ANOMERIC PROTONS IN GLYCOSYLAMINES[a]

Compound	*α Anomer* ($W_{1/2}$ 4 Hz)	*β Anomer* ($J_{1,2}$ 8 Hz)
6	5.20	5.44
7	4.42	4.80
8	4.34	4.76
9	4.38	4.82
10	4.37	4.82
11	4.38	4.80
12	4.41	4.78
13	4.32	4.70
14	5.56	5.90
26	5.50	5.15
27	4.98	unresolved

[a]In pyridine-d_5.

a doublet (J 8 Hz) for H-1β (Table III). Thus, the rule that the chemical shift of the signal for an axial proton is downfield compared with that of the equatorial counterpart is verified with glucose derivatives.

Comparison of the differences ($\Delta\delta$C-1) in ^{13}C-chemical shift for the anomeric carbons of **1** and **3** and of the glycosylamines from β-phenylethylamine and aniline are reported in Table VI. This $\Delta\delta$C-1 value reflects the conformational stability or flexibility of the glycosylamines and is more important when the two anomers are in the same conformation than when they are found mainly in the $^1C_4$ and $^4C_1$ conformations. The $\Delta\delta$C-1 for anomeric pairs of D-ribosylamine (Table VI) is constant or nearly so, but varies for D-glucosylamines.

For the 2,3-*O*-isopropylidene-D-ribosylamines, the $\Delta\delta$C-1 values were in the range 4.63–5.96 p.p.m. (Table II), except for the aminosteroid where the large value (7.03 p.p.m.) is mainly due to the steric hindrance of the steroid skeleton. The $\Delta\delta$ values for the *exo* and *endo* isopropylidene methyl-groups were in the range 1.13–1.86 p.p.m. in Me_2SO-d_6. The ranges were 1.64–1.86 and 1.13–1.42 p.p.m. for the β and α anomers, respectively, and we suggest a limiting lower value of 1.50 p.p.m. for a β anomer. The only recorded example, namely 5-amino-1-(2,3-*O*-isopropylidene-D-ribofuranosyl)imidazole-4-carboxamide[20] has $\Delta\delta$Me values of 1.30 and 1.75 p.p.m., respectively, for the α and β anomers in Me_2SO-d_6, which fall in the range noted above.

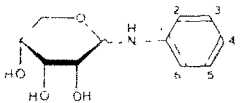
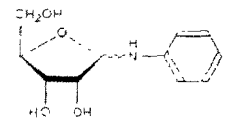
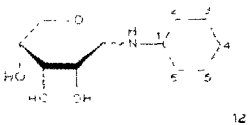
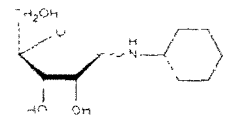
This criterion parallels our rule for determination of the anomeric configuration of nucleosides using ^{1}H-n.m.r. spectroscopy[21]. However, this approach was limited to nucleosides having an aglycon exhibiting anisotropic behaviour[22]. The ^{13}C-chemical shifts of the signals for the isopropylidene methyl groups are mainly the result of a steric, orbital compression, and this new criterion is more general than our previous rule[21]. Furthermore, this approach could be adapted for the determination of the anomeric configuration of *C*-nucleosides, since Moffatt and co-workers[23] reported examples of a correlation between the ^{13}C-chemical shifts of the signals of the methyl groups and the anomeric configuration of *C*-glycosides.

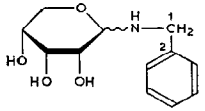
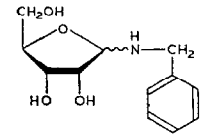
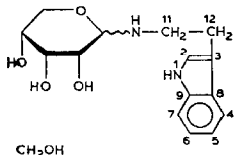
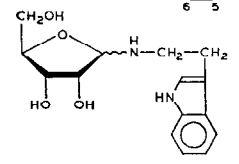
EXPERIMENTAL

General methods. — Melting points were determined with a Gallenkamp apparatus and are uncorrected. T.l.c. was performed on silica gel F-254 (Merck) with detection by u.v. light and charring with sulphuric acid. Column chromatography was performed with silica gel (70–230 mesh, ASTM Merck). Optical rotations were determined with a Perkin–Elmer 241 M.C. polarimeter, and u.v. spectra with an Optica model 10 Spectrometer. ^{1}H-N.m.r. spectra were recorded with a Varian HA-100 spectrometer, and ^{13}C-n.m.r. spectra with Bruker WP-80 or Jeol PS-100 spectrometers for solutions in Me_2SO-d_6 or pyridine-d_5 (internal Me_4Si). Chemical shifts are expressed on the δ scale. Selective decoupling was accomplished by use of monochromatic irradiation at the resonance of the anomeric proton; the frequency was determined from ^{1}H-n.m.r. spectra obtained for the same sample as used for ^{13}C-n.m.r. spectra. Mass spectra were recorded with a Jeol JMS D-100 spectrometer

TABLE IV

PARTIALLY DECOUPLED ^{13}C-N.M.R. DATA[a] FOR **6**, **8**, **10**, AND **12**

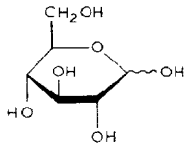
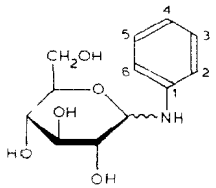
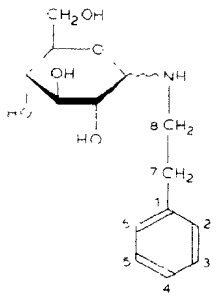
Compound		%	*C-1*	*JC-1*	*C-2*	*C-3*	*C-4*	*C-5*	C_{base}			
									C-1	*C-3,5*	*C-4*	*C-2,6*
	β	45	83.38	0.59	68.91	72.00	72.00	64.90	148.29	129.49	118.20	114.42
	α	45	82.79		69.23	71.64	71.37	64.36	147.10	129.49	118.36	114.51
6												
	β	4	89.98	4.54	76.01	72.37	83.05	63.36				
	α	6	85.44		84.93	n.d.	n.d.	62.81				
									C-1	*C-2,6*	*C-3,5*	*C-4*
	β	87	86.19	0	69.13	73.23	71.41	66.66	52.02	35.54	25.45	25.28
	α		86.19		70.18	72.96	71.59	67.57	53.07	35.41	26.56	24.91
12												
	β	9	95.95	4.97	77.55	72.09	86.31	64.13	54.68			25.37
	α	4	90.98		n.d.[b]	n.d.	84.02	64.88	53.44			25.05

									C-1	*C-2*	*Ph*
	β	40	87.93	−0.09	70.13	71.68	72.69	66.62	50.05	141.68	128.76 127.17
	α	50	88.02		69.13	71.23	72.96	65.48	49.23	141.54	
 8	β	7	95.68	3.26	77.05	72.32	86.00	64.38	49.69		129.36 127.81
	α	3	92.42		n.d.	n.d.	84.78	64.13	50.42		127.49 126.03
									C-11	*C-10*	*C-3,7*
	β	43	88.61	−0.64	69.13	71.82	72.73	66.85	47.36	27.27	112.11; 114.12; 114.30
	α	46	89.25		70.27	71.32	73.19	65.61	47.95	27.38	*C-4,6* 119.18; 119.41 *C-5* 121.83
 10											*C-2*
	β	7.5	96.46	4.20	76.11	72.37	84.82	63.74	47.54		123.29
	α	3.5	92.26		n.d.	n.d.	83.50	63.47	47.86		*C-8* 128.76 *C-9* 137.84

[a]Chemical shifts (δ); solutions in pyridine-d_5. [b]Not determined.

TABLE V

^{13}C-N.M.R. DATA[a] FOR **3**, **26**, AND **27**

Compound		%		*C-1*	*JC-1*	*C-2*	*C-3*	*C-4*	*C-5*	*C-6*	*C_{base}*			
	Me_2SO-d_6	18	β	96.52	3.93	74.86	76.59	70.29	76.44	60.68				
		82	α	92.59		72.66	73.44	70.92	72.02	61.47				
3αP + 3βP														
											C-1	*C-3,5*	*C-4*	*C-2,6*
	Me_2SO-d_6	66.5	β	85.29	2.45	73.14	77.74	70.41	77.28	61.17	147.26	128.81	117.56	113.83
		33.5	α	82.84		71.18	73.60	70.77	71.18	61.17	147.69		117.20	113.33
26αP + 26βP	C_5D_5N	64	β	86.47	1.88	74.60	79.35	71.54	78.62	62.42	148.11	129.54	118.77	114.89
		36	α	84.59		71.51	72.41	71.91	72.18	62.56	148.25		118.31	114.44
											C-8	*C-7*	*C-1*	*Ph*
		96	β	90.71		73.54	77.74	70.57	77.49	61.40	47.60	36.38	140.65	128.80
27αP + 27βP	Me_2SO-d_6				3.93									128.36
		4	α	86.78		n.d.[b]	n.d.	n.d.	n.d	n.d.				125.97
		83	β	92.12		75.20	79.26	72.14	79.26	63.15	48.55	37.51	141.13	129.31
	C_5D_5N				3.80									126.31
		17	α	88.32		72.64	75.79	72.64	73.14	63.33	48.23	37.00	141.22	123.81

[a]Chemical shifts (δ). [b]Not determined.

TABLE VI

$\Delta\delta$C-1 VALUES FOR **6**, **9**, **26**, AND **27**

Compound	*Solvent*	*Anomer*	*δC-1 sugar*	*δC-1 NH-CH₂-CH₂φ (A)*	*NHφ (B)*	*ΔδC-1 (A-B)*	*ΔδC-1 (β-α)*	
1	$(CD_3)_2SO$	β	94.50				0.78	
		α	93.72					
3	$(CD_3)_2SO$	β	96.52				3.93	
		α	92.59					
9 and **6**	$(CD_3)_2SO$	β		86.52	81.59	5.42	0.28	0.34
		α		86.24	81.25	3.94		
27 and **26**	$(CD_3)_2SO$	β		90.71	85.29	4.93	3.93	2.45
		α		86.78	82.84	4.99		
9 and **6**	Pyridine-d_5	β		89.20	83.38	5.65	0.59	0.59
		α		88.61	82.79	3.73		
27 and **26**	Pyridine-d_5	β		92.12	86.47	5.82	3.80	1.88
		α		88.32	84.59	5.82		

by the direct-insertion procedure. Analyses were performed by the Service Central de Micro-Analyse du CNRS.

Synthesis of D-*ribosylamines*. — Physical data are reported in Table VII.

Process A. To a solution of dry D-ribose (**1**; 2 g, 13 mmol) or 2,3-*O*-isopropylidene-D-ribofuranose[24] (**2**; 2 g, 10 mmol) in the minimum amount of anhydrous methanol was added a stoichiometric amount of freshly purified amine. The mixture was stirred at room temperature for the time noted in Table VII. The reaction mixture was then subjected to short-column chromatography on silica gel, or the product was crystallised.

Process B. The reaction mixture as in A was boiled under reflux.

Process C. As in B, but with anhydrous ethanol as the solvent.

2,3,5-Tri-O-*acetyl*-D-*ribofuranose* (**4**). — This compound was obtained as an oil by the literature[16] procedure and had $[\alpha]_D^{20}$ +45° (*c* 1, water).

2,3,4-Tri-O-*acetyl*-D-*ribopyranose* (**5**). — To a solution of 2,3,4-tri-*O*-acetyl-D-ribopyranosyl bromide[25] (3 g, 9 mmol) was added cold distilled water (10 mL), and the solution was stirred at 0° for 1 h and then extracted with chloroform (3 × 200 mL). The combined extracts were washed with cold, saturated, aqueous sodium hydrogencarbonate (20 mL) and then water (2 × 100 mL), dried (Na_2SO_4), and concentrated *in vacuo*. The oily residue (2.25 g) was purified by column chromatography (chloroform–methanol, 9.5:0.5), to give **5** (2.15 g, 86%) as an oil, $[\alpha]_D^{20}$ −16° (*c* 1, water), R_F 0.6 (acetone-chloroform, 1:1). P.m.r. data ($CDCl_3$): δ 3.59 (q, 1 H, $J_{5e,5a}$ 11.4 Hz, H-5*a*), 3.92 (q, 1 H, $J_{4,5e}$ 6.6 Hz, H-5*e*), 4.90 (d, 1 H, $J_{1,2}$

TABLE VII

Compound	*Method*	*Yield (%)*	*M.p. (degrees)*	R_F *(T.l.c.)*	*Crystallisation solvent*	$[\alpha]_D^{20}$ *(c 1) (degrees)*	*Formula*	*Analysis (%) C H N Calc. Found*			λ_{max}^{EtOH} *(nm) (ε)*
6	*A* (16 h)	100	135–136	0.41 ($CHCl_3$–MeOH, 8.5:1.5)	MeOH	+129 (pyridine)	$C_{11}H_{15}NO_4$	58.66 58.54	6.71 6.70	6.22 6.18	283 (1977) 236 (14,299)
	B		130–132			+174 (pyridine)					
	C		125–126			+60 (pyridine)					
9	*A* (17 h)	80	107–109	0.45 ($CHCl_3$–MeOH, 5:5)	Et_2O	−4 (MeOH)	$C_{13}H_{19}NO_4$	61.66 61.68	7.50 7.58	5.33 5.40	257 (19,930)
10	*A* (1 h)	89	129–130 (dec.)	0.40 (AcOEt–MeOH, 7:3)	MeOH	+21 (Me_2SO)	$C_{15}H_{20}N_2O_4$	61.63 61.52	6.89 6.67	9.58 9.59	221 (38,710) 283 (7,740) 290 (6,450)
11	*A* (60 h)	57	Oil	0.41 ($CHCl_3$–MeOH, 5:5)			$C_{11}H_{23}NO_6$	49.44 49.61	9.33 8.68	5.24 5.29	
12	*A* (1 h)	100	107–109	0.45 ($CHCl_3$–MeOH, 5:5)	MeOH	−9 (MeOH)	$C_{11}H_{21}NO_4$	57.12 57.16	9.15 9.17	6.06 5.93	
13	*A* (4 h)	70	109–110	0.30 (CH_2Cl_2–MeOH, 9.6:4)	MeOH	−39 (MeOH)	$C_{21}H_{39}NO_5 \cdot 0.5CH_3OH$	67.25 67.32	9.44 9.34	3.20 3.19	

14	*A* (42 h)	42	166–168	0.31 ($CHCl_3$–MeOH, 7:3)	MeOH	+7 (Me_2SO)	$C_9H_{14}N_4O_5$	41.86 41.82	5.46 5.52	21.70 21.39	270 (12,596) 231 (4,799) (H_2O)
17	*B* (78 h)	70	98–100	0.41 ($CHCl_3$–MeOH, 9:1)	CCl_4	+52 (pyridine)	$C_{14}H_{19}NO_4$	63.38 63.53	7.22 7.14	5.28 5.28	282 (3,230) 236 (19,091)
19	*A* (60 h)	86	72–74	0.35 ($CHCl_3$–MeOH, 9.5:0.5)	Ether–cyclohexane (1:2)	−51 (MeOH)	$C_{15}H_{21}NO_4$	64.49 64.20	7.58 7.63	5.01 5.02	262 (8,780)
20	*A* (3 days)	100	92–93	0.51 ($CHCl_3$–MeOH, 9:1)	Ether	−34 (MeOH)	$C_{16}H_{23}NO_4$	65.52 65.33	7.84 7.89	4.77 4.83	257 (19,930)
21	*A* (4 days, N_3)	62	73–75	0.30 ($CHCl_3$–MeOH, 9.5:0.5)	EtOH–Et_2O	−59 (Me_2SO)	$C_{18}H_{24}N_2O_4$	65.04 64.97	7.27 7.18	8.43 8.43	221 (34,805) 280 (6,060) 290 (5,108)
22	*C* (17 h)	52	Oil	0.45 ($CHCl_3$–MeOH, 9.6:0.4)		−6 (Me_2SO)	$C_{14}H_{27}NO_6$	53.00 53.02	8.84 8.88	4.58 4.47	
23	*B* (10 h)	82	84–86	0.54 ($CHCl_3$–MeOH, 9.6:0.4)	$CHCl_3$–Pentane (1/2)	−7 (MeOH)	$C_{14}H_{25}NO_4$	61.97 62.00	9.28 9.02	5.16 5.23	
24	*A* (4 days)	52	134–136	0.44 (CH_2Cl_2–MeOH, 9.5:0.5)	MeOH	−59 (MeOH)	$C_{27}H_{43}NO_5$	70.25 70.30	9.39 9.25	3.03 3.00	
25	*C* (30 h)	50	146–148	0.30 ($CHCl_3$–MeOH, 4:1)	H_2O	−6 (Me_2SO)	$C_{12}H_{18}N_4O_5 \cdot H_2O$	45.61 45.77	6.39 6.38	17.73 17.72	272 (11,100) 235 (4,840)

5 Hz, H-1), 5.03 (m, 2 H, $J_{3,4}$ 3.5, $J_{4,5a}$ 3.6 Hz, H-2,4), 5.33 (t, $J_{2,3}$ 3.5 Hz, H-3), and 6.97 (d, $J_{1,OH}$ 5.5 Hz).

Anal. Calc. for $C_{11}H_{16}O_8$: C, 47.83; H, 5.84. Found: C, 47.69; H, 5.93.

D-*Ribopyranosylamine* (**7**). — This compound was prepared following the procedure of Cusack *et al.*[6], and had m.p. 128 °; lit.[6] m.p. 128–129 °.

N-*Benzyl*-D-*ribosylamine* (**8**). — This compound was synthesised by process *A* (2 h). The crude solution was concentrated under reduced pressure, the resulting oil (quantitative yield) could not be crystallised or chromatographed without rapid degradation, thereby precluding the usual analysis. The compound had R_F 0.42 (chloroform–methanol, 7:3). Mass spectrum: *m/z* 239 (M^+ — H_2O).

4-Carbamoyl-5-D-*ribosylamino-imidazole* (**14**). — This compound was synthesised by procedure *A*, chromatographed on silica gel (40 g, 1.5 g of compound; chloroform–methanol, 8.5:1.5), and then crystallised from methanol at 0 °.

2,3,5-Tri-O-*acetyl*-N-*phenyl*-D-*ribofuranosylamine* (**15**). — A mixture of **4** (4.1 g, 15 mmol) and aniline (1.38 g, 15 mmol) in anhydrous ethanol (20 mL) was heated at 50 ° overnight, and then concentrated to dryness. The oily residue was purified by column chromatography (chloroform–methanol, 99.5:0.5), to give **15** as an oily, anomeric mixture (49 %; $\alpha\beta$-ratio, 2:3 in $CDCl_3$), $[\alpha]_D^{20}$ ~0 ° (*c* 1, chloroform), R_F 0.6 (chloroform–methanol, 9.5:0.5). ^{13}C-N.m.r. data ($CDCl_3$): δ 20.68 (Me), 86.36 (C-1β), 83.78 (C-1α), 78.32 (C-4β), 77.64 (C-4α), 73.35 (C-2β), 71.60 (C-2α), 71.10 (C-3β), 70.18 (C-3α), 63.93 (C-5β), 63.39 (C-5α), 114.51 (Ph, C-2,6), 119.68 (Ph, C-4α), 119.92 (Ph, C-4β), 129.38 (Ph, C-3,5), 144.94 (Ph, C-1β), 145.55 (Ph, C-1α), 169.23, 169.62, 169.86, 170.05, 170.59 (C = O).

Anal. Calc. for $C_{17}H_{21}NO_7$: C, 58.15; H, 5.98; N, 3.99. Found: C, 57.77; H, 6.00; N, 4.14.

2,3,4-Tri-O-*acetyl*-N-*phenyl*-D-*ribopyranosylamine* (**16**). — The above procedure was used with **5** (1 g, 3.6 mmol) and aniline (0.337 g, 3.6 mmol) in anhydrous ethanol (5 mL). The oily residue was purified by column chromatography (chloroform–acetone, 1:1), to give **16** as an oily, anomeric mixture (75 %; $\alpha\beta$-ratio, 1:4 in $CDCl_3$), $[\alpha]_D^{20}$ ~0 ° (*c* 1, chloroform), R_f 0.65 (chloroform–methanol, 9.5:0.5). ^{13}C-N.m.r. data ($CDCl_3$): 20.77 (Me), 81.39 (C-1β), 79.73 (C-1α), 68.76 (C-2,4β), 68.72 (C-4α), 67.25 (C-2α), 66.76 (C-3β), 66.18 (C-3α), 61.84 (C-5β), 59.08 (C-5α), 114.26 (Ph, C-2,6), 119.69 (Ph, C-4), 129.34 (Ph, C-3,5), 144.60 (Ph, C-1α), 144.89 (Ph, C-1β), 169.52, 169.76, 169.91, 170.54 (C = O).

Anal. Calc. for $C_{17}H_{21}NO_7$: C, 58.15; H, 5.98; N, 3.99. Found: C, 57.83; H, 5.95; N, 4.09.

Acetylation of **6**α*P and* **6**α*P* + **6**βP. — This reaction was performed following the literature[15a] procedure.

Deacetylation of **16**. — To a solution of **16** (1.76 g, 0.005 mol) in anhydrous methanol (5 mL) was added M methanolic sodium methoxide (0.5 mL). The mixture was kept at room temperature for 1.5 h, neutralised with solid CO_2, filtered, and concentrated under diminished pressure. The solid residue was crystallised from anhydrous methanol, to give **6**αP (0.95 g, 85 %)

2,3-O-Isopropylidene-D-ribofuranosylamine (**18**). — This compound was synthesised[6] by the action of 0.15M methanolic sodium methoxide (3 mL) on 2,3-*O*-isopropylidene-*N*-tosyl-D-ribofuranosylamine (0.5 g, 1.4 mmol). The mixture was neutralised with solid CO_2, filtered through Celite, and concentrated under diminished pressure, to give amorphous **18** (0.2 g), which rapidly decomposed on attempted purification, thus precluding the usual analyses. It has R_F 0.42 (chloroform–methanol, 8.5:1.5). Mass spectrum: *m/z* 189 ($M^{+}\cdot$).

N-*2,2-Diethoxyethyl-2,3-O-isopropylidene-D-ribofuranosylamine* (**22**). — This compound was synthesised by procedure *C*, and chromatographed on neutral alumina 90 (Merck, Activity I, 70–230 mesh ASTM, 25 g/g of product) with chloroform–methanol (9.6:0.4).

N-*Phenyl-D-glucopyranosylamine* (**26**). — A mixture of D-glucose (3 g, 17 mmol), aniline (1.55 g, 17 mmol), and anhydrous ethanol (50 mL) was boiled under reflux for 16 h and then stored at 4° overnight, to give **26** (3.8 g, 89%), m.p. 138–140°, $[\alpha]_D^{20}$ +14° (*c* 1, methanol); lit.[19] m.p. 140°, $[\alpha]_D^{16}$ +10.5° (*c* 0.8, methanol).

N-*2-Phenylethyl-D-glucopyranosylamine* (**27**). — A solution of D-glucose (9 g, 0.05 mol) and 2-phenylethylamine (12.1 g, 0.1 mol) in anhydrous methanol (20 mL) was stirred overnight at room temperature and then poured dropwise into anhydrous ether (200 mL) with vigourous stirring, to give **27** (11 g, 75%), m.p. 94–96°, $[\alpha]_D^{20}$ −21.5° (*c* 1, methanol); lit.[7a] m.p. 89°, $[\alpha]_D^{20}$ −25° (*c* 1, methanol).

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