commercially available 7-acetoxynorbornadiene followed by treatment with methyllithium) was added to a mixture of 3.0 g of triflic anhydride in 15 mL of pyridine at 0 °C. After 90 min at 0 °C a standard aqueous workup was used to isolate 11. Ether was used for extractions. After solvent removal by rotary evaporator, the residue was distilled to give 1.40 g (64%) of triflate 11:[24b] bp 63–65 °C (3 mm); NMR (300 MHz) ($CDCl_3$) δ 4.97 (1 H, brs), 2.38 (2 H, m), 1.92 (2 H, m) 1.65 (2 H, m), 1.44 (2 H, AB q), 1.33 (2 H, AB q).

Reaction of 7-Norbornyl Triflate (11) with Potassium Diethyl Phosphite. 7-Norbornyl triflate (0.60 g) was added to a solution of potassium diethyl phosphite prepared from 0.19 g of potassium and 0.68 g of diethyl phosphite in 100 mL of ammonia. After vigorous stirring of the mixture for 20 min, the triflate dissolved. Gas chromatographic analysis showed no reaction after 10 h at −33 °C. Samples of the solution were sealed in tubes. After 1 day at room temperature, no reaction was apparent. A sample (sealed tube) was then placed in a steel bomb, and liquid ammonia was introduced into the cooled bomb. After sealing, the bomb was placed in a bath and maintained at 65 °C for 35 h. After cooling, the bomb was opened and the tube was removed. After being cooled in dry ice, the tube was opened, and an aqueous workup followed. No phosphate ester **12** was present by gas chromatographic analysis. Much of the triflate **11** had been consumed. Two products of shorter gas chromatographic retention time than **11** were observed along with unreacted **11**. Samples of each product were isolated by preparative gas chromatography. The major product, which could be extracted with dilute hydrochloric acid, was identified as 7-norbornyl amine. The minor product was identified as bicyclo[2.2.1]heptan-7-ol by comparison with an authentic sample.[25]

Reaction of Phenyl Triflate (5a) with Potassium Diethyl Phosphite in the Presence of *p*-Methylphenoxide. A solution of potassium diethyl phosphite in 170 mL of liquid ammonia was prepared as previously described from 0.55 g of potassium and 1.95 g of diethyl phosphite. Potassium (0.26 g) was then added followed by 0.72 g of *p*-cresol. The color was discharged. Phenyl triflate (**5a**, 1.50 g) was then added, and samples were periodically withdrawn, diluted with ether, and extracted with water. The ether extracts were analyzed by gas chromatography. Both phosphates **6a** and **6b** were present. Figure 1 gives the area percent of phosphate **6a** as a function of time. After 17 h, the ratio of **6a** to **6b** was 45:55.

Reaction of 2,6-Dimethylphenyl Triflate (5e) with Potassium Diethyl Phosphite in the Presence of 2,4,6-Trimethylphenoxide. A solution of potassium diethyl phosphite in 170 mL of ammonia was prepared as previously described from 0.55 g of potassium and 1.95 g of diethyl phosphite. Potassium (0.27 g) was added followed by 0.93 g of 2,4,6-trimethylphenol. 2,6-Dimethylphenyl triflate (**5e**, 1.74 g) was added, and the mixture was stirred vigorously for 5 min to dissolve the triflate **5e**. Samples were periodically withdrawn and diluted with ether, and water was added. The ether extracts were analyzed by gas chromatography. After 8 min greater than 99.7% of the product was phosphate **6e**. After 30 min, about 99% of the product was **6e** and 1% of 2,4,6-trimethylphenyl diethyl phosphate had appeared. After 1 h, 2% of this product was present and 8% after 5 h. On completion of the reaction (25 h) the ratio of phosphate **6e** to 2,4,6-trimethylphenyl phosphate was 88:12.

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Registry No. **5a**, 17763-67-6; **5b**, 29540-83-8; **5c**, 32578-31-7; **5d**, 86364-01-4; **5e**, 86364-02-5; **5f**, 66107-29-7; **5g**, 29540-84-9; **5h**, 86364-03-6; **5i**, 86364-04-7; **5** (R = *p*-formyl), 17763-69-8; **6a**, 2510-86-3; **6b**, 4877-08-1; **6c**, 14143-01-2; **6d**, 16462-76-3; **6e**, 39604-15-4; **6f**, 5076-68-6; **6g**, 5076-63-1; **6h**, 32019-36-6; **6i**, 22955-88-0; **7**, 28075-50-5; **8**, 4452-32-8; **9**, 25327-17-7; **10**, 86364-05-8; **11**, 25354-43-2; **12**, 86364-06-9; *p*-toluenesulfonic acid, 104-15-4; *exo*-bicyclo[3.1.0]hexan-6-ol, 13830-42-7; *endo*-bicyclo[3.1.0]hexan-6-ol, 13830-09-6; triflic anhydride, 358-23-6; bicyclo[2.2.1]heptan-7-ol, 2566-48-5; 7-acetoxynorbornadiene, 13426-49-8; potassium *p*-methylphenoxide, 1192-96-7; potassium 2,4,6-trimethylphenoxide, 79719-34-9; 2,4,6-trimethylphenyl diethyl phosphate, 67951-88-6; potassium diethyl phosphite, 54058-00-3.

Conformational and Configurational Studies on *N*-(Substituted phenyl)pyranosylamine Derivatives by High-Resolution Nuclear Magnetic Resonance Spectroscopy[1]

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A series of *N*-(substituted phenyl)-tri-*O*-acetyl-D-xylopyranosylamines (Ia–h) and *N*-(para-substituted phenyl)per-*O*-acetylglycopyranosylamines, including four hexose derivatives (D-glucose, II; D-galactose, III; D-mannose, IV; and L-rhamnose, V) and two pentose derivatives (D-arabinose, VI; D-ribose, VII), has been synthesized and characterized by 270- and 500-MHz NMR spectroscopy. The configuration and conformation of these carbohydrate derivatives were determined by analyzing the chemical shifts and coupling constants by NMR spectroscopy. Most of the synthesized compounds were found to exist in the *C*1 (D) conformation, with the exception of the rhamnosyl and arabinosyl derivatives V and VI which favored the 1*C* (L) and 1*C* (D) conformations, respectively. Compounds Ia–h, II, and III existed in the β configuration, and the rest of the compounds (IV–VII) favored the α configuration.

A series of *N*-glycopyranosylamines has been synthesized,[3a-c] with the objective being the development of agents capable of modifying the biosynthesis of glycosaminoglycans by serving as artificial acceptors for biosynthetic

(1) Presented in part at the 183rd National Meeting of the American Chemical Society. See: Wang, L.; Lin, T.-S.; Sartorelli, A. C. In "Abstracts of Papers", 183rd National Meeting of the American Chemical Society, Las Vegas, NV, March 28–April 2, 1982; American Chemical Society: Washington, DC; Abstract CARB 54.

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(3) (a) Presented in part at the 182nd National Meeting of the American Chemical Society. See: Wang, L.; Maniglia, C. A.; Mella, S. L.; Sartorelli, A. C. In "Abstracts of Papers", 182nd National Meeting of the American Chemical Society, New York, New York, Aug 23–28, 1981; American Chemical Society: Washington, DC; Abstract CARB 23. (b) Wang, L.; Maniglia, C. A.; Mella, S. L.; Sartorelli, A. C. *J. Med. Chem.* **1983**, *26*, 629. (c) Wang, L.; Maniglia, C. A.; Mella, S. L.; Sartorelli, A. C. *J. Med. Chem.*, in press.

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enzymes. To correlate structural parameters with the effects of these agents on glycosaminoglycan biosynthesis, it was necessary to characterize the structure of these derivatives. The use of NMR spectroscopy for configurational and conformational analysis of substituted tetrahydropyran ring systems was initiated by Lemieux and co-workers.[4] Their studies indicated that for six-membered-ring compounds, axial protons usually resonate at higher field than equatorial protons, while axial acetylmethyl protons usually resonate at lower field than equatorial acetylmethyl protons. In addition, the spin–spin coupling constant between neighboring hydrogen atoms in the axial orientation is about 2 to 3 times larger than those of neighboring hydrogens in other orientations. Therefore, by measurement of the chemical shift and the magnitudes of the spin coupling constants, it is possible to determine favored conformations and configurations of various aldopyranoses and their derivatives.

A survey of the literature in this area has shown that many investigators have conducted conformational and configurational analyses of acetylated aldopyranosyl halides,[5-7] acetates,[8-12] and acetylated alkyl aldopyranosides[13,14] by NMR spectral analysis. However, only a few conformational and configurational analyses on *O*-acetyl- and *O*-benzylglycosylamines have been reported.[15-21]

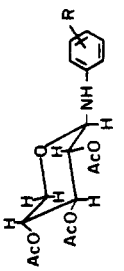
The present study describes an analysis of the NMR spectra of 14 *N*-(substituted phenyl)per-*O*-acetylated-D-glycopyranosylamine derivatives (Ia–h, II–VII). These compounds existed in thermodynamically stable anomeric forms.

Experimental Section

N-(Substituted phenyl)per-*O*-acetyl-D-glycopyranosylamines, including four hexose derivatives (D-glucose, II; D-galactose, III; D-mannose, IV; L-rhamnose, V) and two pentose-containing compounds (D-arabinose, VI; D-ribose, VII), were prepared by acetylating the corresponding *N*-(substituted phenyl)-pyranosylamines which were, in turn, obtained by condensation of various amine compounds with different monosaccharides. The synthesis and biological activity of these compounds will be published elsewhere.[3b,c]

Unless otherwise indicated, NMR spectra were measured at either 270 or 500 MHz (Brucker HX-270 or WM-500 superconducting spectrometer equipped with a Brucker ASPECT 2000 computer by using freshly prepared samples in $CDCl_3$ solution (1%, w/v) with tetramethylsilane as the internal standard; spectra were taken immediately after preparation of samples. The chemical shifts were obtained by analysis of spectra on a first-order basis, and are considered accurate to within ±0.001 ppm. All of the coupling constants were also obtained on a first-order basis as direct peak-openings from the spectra measured at a sweep

Table I. Chemical Shifts[a] of Methine and Methylene Protons of *N*-(Substituted phenyl)-tri-*O*-acetyl-β-D-xylopyranosylamines in Chloroform-*d*



compd	R	chemical shifts,[b] δ									
		H-1	H-2	H-3	H-4	H-5e	H-5a	NH	$COCH_3$	$COCH_3$	$COCH_3$ $COOCOCH_3$
Ia	*p*-H	4.76 t	4.98 t	5.36 t	5.03 sx	4.10 q	3.42 t	4.70 d	2.04	2.05	2.06
Ib	*p*-CH_3	4.67 t	4.97 t	5.36 t	5.04 sx	4.09 q	3.41 t	4.51 d	2.04	2.05	2.06
Ic	*p*-OCH_3	4.63 t	4.96 t	5.34 t	5.05 sx	4.09 q	3.39 t	4.35 d	2.05[c]	2.05[c]	2.06
Id	*p*-Cl	4.61 t	4.99 t	5.35 t	5.04 sx	4.09 q	3.41 t	4.69 d	2.05[c]	2.05[c]	2.06
Ie	*p*-$COOC_2H_5$	4.75 t	4.99 t	5.37 t	5.03 sx	4.12 q	3.45 t	5.12 d	2.05	2.06	2.07
If	*p*-SO_2NH_2[d]	5.13 t	4.97 t	5.34 t	4.93 sx	4.01 q	3.66 t	6.23 d	2.03	2.04	2.05
Ig	*p*-$COCOCH_3$	4.76 t	4.99 t	5.38 t	5.04 sx	4.13 q	3.47 t	5.34 d	2.07[c]	2.07[c]	2.08 2.35
Ih	*o*-$COCOCH_3$	4.93 t	5.10 t	5.30 t	4.99 sx	4.15 q	3.53 t	8.35 d	2.13	2.09	2.07 2.36

[a] Data obtained from spectra measured at 270 MHz. [b] Observed multiplicities: d, doublet; q, quartet; sx, sextet; t, triplet. [c] Six-proton singlet. [d] In acetone-d_6.

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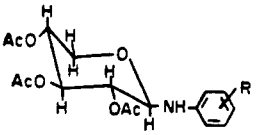
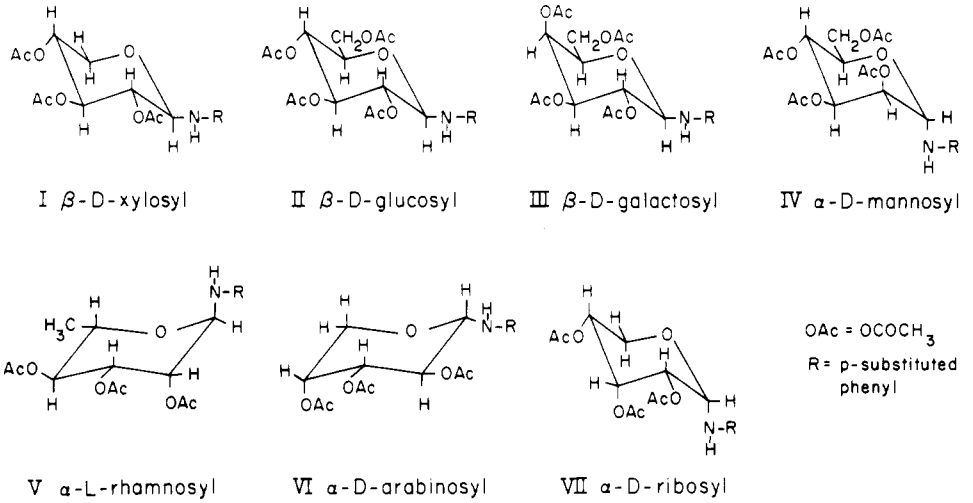
Table II. Coupling Constants of Methine and Methylene Protons for N-(Substituted phenyl)-tri-O-acetyl-β-D-xylopyranosylamines in Chloroform-d



compd	R	coupling constants,[a,c] Hz						
		$J_{1,NH}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5a}$	$J_{4,5e}$	$J_{5a,5e}$
Ia	p-H	7.96	8.85	9.07	9.51	9.63	5.75	−11.50
Ib	p-CH_3	9.77	9.28	9.28	9.53	10.12	5.63	−11.48
Ic	p-OCH_3	8.10	8.30	9.04	9.53	9.29	5.62	−11.48
Id	p-Cl	7.07	8.85	8.86	9.51	9.20	5.71	−11.50
Ie	p-$COOC_2H_5$	8.79	8.79	9.28	9.52	9.78	5.86	−11.72
If	p-SO_2NH_2[b]	8.10	9.14	8.93	9.55	9.15	5.61	−11.82
Ig	p-$COOCOCH_3$	8.40	8.85	9.07	9.51	9.74	5.75	−11.50
Ih	o-$COOCOCH_3$	7.32	7.33	7.33	7.81	8.30	4.88	−12.20

[a] Data obtained from spectra measured at 270 MHz. [b] In acetone-d_6. [c] Abbreviations: a, axial; e, equatorial.

Chart I. Conformation and Configuration of Sugar Moieties



width of 270 or 500 Hz. These values were calculated by a computer and were considered to be accurate within ±0.1 Hz. Spectral data for the 14 compounds (Ia–h, II–VII) are tabulated in Tables I–IV.

Results and Discussion

Analysis of NMR spectra indicated that all of the 14 compounds synthesized (Ia–h, II–VII) existed predominantly in the chairlike configuration and conformation as shown in Chart I. In general, the anomeric protons (H-1) of acetylated aldopyranosyl halides[5-7] and acetates[8-12] and acetylated 1-thioaldopyranoses[22] were at relatively lower field than other sugar ring protons. This presumably was due to the deshielding effects of the 1-substituted halogen and/or the acetyl group of the molecule.[5,11] In these cases, the H-1 signal can be treated as the X portion of an AX system, where A is H-2, or as the X portion of an AA'X system;[23] when H-2 and H-3 are strongly coupled and demonstrate little difference in chemical shift, the coupling constant of J_{AX} between H-1 and H-2 is critical for determining anomeric configuration and ring conformation.

In the present study of acetylated N-(substituted phenyl)xylo- and glycopyranosylamine derivatives (Ia–h and II–VII, respectively), it was found that the H-3 signals in Ia–h, II, and VII appeared at lower field (δ 5.30–5.59) than those of other sugar ring protons. None of the signals of the anomeric proton (H-1) in compounds Ia–h, II–VII were at the lowest field compared with other sugar protons. This was probably due to a weaker deshielding effect by the 1-substituted phenylamino group. The shift to higher field of the H-1 signal causes it to appear within the "envelope" of signals for H-2,3,4 and 1-NH in the spectra of this series of compounds. Thus, first-order interpretations of this region of the spectra of the pyranosylamine derivatives were more difficult than those of the corresponding 1-halo and acetyl analogues. Furthermore, the H-1 proton was not only coupled with the H-2 proton but also further coupled with the neighboring 1-NH proton; thus, the H-1 signal pattern of the anomeric protons in this series of compounds are more complicated than other acetylated aldopyranosyl halides[5-7] and acetates.[8-12] In addition, the 1-NH doublets also appeared in this region; therefore, the first-order interpretations of the spectra of compounds Ia–h were more complicated than those of the acetylated aldopyranose derivatives.[5-11]

The identification and analysis of the H-1 anomeric protons were achieved by either deuterium exchange or spin–spin decoupling techniques.

N-(Substituted phenyl)-tri-O-acetyl-β-D-xylopyranosylamine Derivatives (Ia–h). The xylopyranosylamine derivatives that were evaluated (Ia–h) contained different substituents in the benzene ring at the para position, except for Ih where the ortho position was substituted by a $COOCOCH_3$ group. The C-5 methylene

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Table III. Chemical Shifts[a] of Methine and Methylene Protons for the *N*-(*p*-Substituted phenyl)-*O*-peracetylglycopyranosylamines in Chloroform-*d*

compd	R	R'	chemical shift,[b] δ											
			H-1	H-2	H-3	H-4	H-5	H-6[c]	H-6'[c]	NH	$COCH_3$	$COCH_3$	$COCH_3$	$COCOCH_3$
II	β-D-gluco	H	4.81 t	5.07 t	5.41 t	5.10 t	3.87 o	4.32 q	4.12 q	5.30 d	2.07	2.07	2.06	2.05
II	β-D-galacto	H	4.81 t	5.26 t	5.20 q	5.49 d	4.07 t	4.19 q	4.13 q	5.37 d	2.17	2.08	2.06	2.03
IV	α-D-manno	$COCH_3$	5.05 br d	5.54 d	5.17 q	5.29 t	3.87 o	4.33 q	4.12 q	5.35 d	2.30	2.08	2.07	2.03
V	α-L-rhamno[d,e]	H	5.04 d	5.52 q	5.13 q	5.09 q	3.69 o			4.99 d	2.28	2.09	2.09	

compd	R	R'	chemical shift,[b] δ							$COCH_3$	$COCH_3$	$COCOCH_3$
			H-1	H-2	H-3	H-4	H-5[c]	H-5'[c]	NH			
VI	α-D-arabino	H	4.75 t	5.21 q	5.39 br s	5.39 br s	4.05 q	3.79 q	5.26 d	2.17	2.08	2.06	
VII	α-D-ribo[d]	$COCH_3$	5.26 q	5.29 t	5.59 br s	5.10 qu	3.94 q[f]	3.67 q[f]	5.59 br s	2.22	2.13	2.10	2.35

[a] Data obtained from spectra measured at 270 MHz. [b] Observed multiplicities: br s, broad singlet; br d, broad doublet; d, doublet; o, octet; q, quartet; qu, quintet; t, triplet. [c] The C-5 and C-6 protons resonating at lower field are designated H-5 and H-6, respectively, and those resonating at higher field are designated H-5' and H-6', respectively. [d] Data obtained from spectra measured at 500 MHz. [e] C-5 CH_3 (δ 1.29 d). [f] H-5a. [g] H-5e.

protons were observed as a seven-line AB pattern in an ABXY system. The triplets at the higher field were assigned to the axial H-5 protons in the *C*1 conformation on the basis of the large coupling constants with H-4 ($J_{4,5a}$ = 8.32–10.12 Hz). The quartets at lower field were assigned to the H-5 equatorial protons on the basis of their smaller coupling constants ($J_{4,5e}$ = 4.88–5.86 Hz). The $J_{4,5e}$ couplings were larger than those normally observed for vicinal protons in a gauch relationship; however, relatively large $J_{4,5e}$ couplings have been reported with methyl tri-*O*-acetyl-β-D-xylopyranoside[13] and α-D-xylopyranose tetraacetate.[12]

The identification of the anomeric proton was achieved by both the exchange of the 1-NH proton with D_2O for compounds Ia–d,f,g and by spin decoupling for compounds Ie and Ih where the exchange did not occur. Upon deuterium exchange, the triplet of the anomeric proton collapsed to a doublet and simultaneously the doublet of the 1-NH disappeared. Of the remaining two triplets (Table I), one at the lowest field (δ 5.30–5.38) was assigned to H-3. This resembles the H-3 signal of methyl tri-*O*-acetyl-β-D-xylopyranoside reported by Durette.[13] The other signal was assigned to H-2 (δ 4.96–5.10). The multiplet at δ 4.93–5.03, observed as a six-line pattern, was assigned to H-4.

All of these compounds had a rather large coupling constants of $J_{1,2}$, $J_{2,3}$, $J_{3,4}$, and $J_{4,5}$ (Table II). This finding indicated an axial orientation of hydrogen atoms at C1–C4, and the existance of the favored *C*1 (D) conformation and the β configuration. The ortho derivative Ih showed a somewhat smaller coupling constant for the vicinal protons, in comparison with the corresponding para derivatives Ia–g. Thus, the possibility of the existance of a small proportion of the alternative all-axial 1*C* conformation for 1h cannot be excluded.

The acetoxy group signals of these compounds (Table I) provided further verification of the favored *C*1 (D) conformation and β configuration of Ia–h, since these signals fell within the range expected for equatorial secondary acetoxy groups.[4,24,25]

Influence of Substituents in Compounds Ia–h on the Chemical Shifts of Protons. The substituent groups in the aromatic benzene ring had, in general, little effect on the observed chemical shifts of the sugar ring protons, except for protons H-1 and 1-NH which are closely linked to the carbohydrate. All of the H-1 signals appeared at higher field than H-2, H-3, and H-4, except for compound If, and chemical shifts were related to the electronic nature of the substituent group of the benzene ring; the electron-donating groups caused an upfield shift compared to that of the parent compound Ia, while electron-withdrawing groups caused a downfield shift (Figure 1). The substituent group also exerted major effects on the chemical shift of the 1-NH protons. Electron-donating substituents directed the 1-NH signal upfield; for example, in compound Ic, the 1-NH signal was 0.35 ppm more upfield than in the unsubstituted compound Ia, while in the presence of electron-withdrawing groups, such as in compound If and Ig, the chemical shifts of the 1-NH proton moved downfield about 1.53 and 0.64 ppm, respectively. Furthermore, it was of interest that in compound Ih, the 1-NH proton was shifted to the lowest field (Figure 2); thus, in comparison to the parent compound Ia, the NH proton in Ih was observed to be 3.65 ppm downfield, and compared to the corresponding para derivatives, the shift

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Table IV. Coupling Constants of Methine and Methylene Protons for N-(p-Substituted phenyl)-O-peracetylglycopyranosylamines in Chloroform-d

compd[h]	R	R'	coupling constants,[a] Hz $J_{1,NH}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{5,6}$	$J_{5,6'}$	$J_{6,6'}$
II	β-D-gluco	H	8.85	9.07	9.07	9.51	10.16	5.53	1.99	−12.50
III	β-D-galacto	H	8.79	8.30	9.24	3.42	2.44	6.35	6.35	−10.62
IV	α-D-manno	$COCH_3$	8.72	c	3.32	9.97	9.34	6.02	2.49	−12.35
V	α-L-rhamno[d,e]	H	9.14	0.89	2.93	9.64	10.10			

compd	R	R'	coupling constants,[a] Hz $J_{1,NH}$	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$[b]	$J_{4,5'}$[b]	$J_{5a,5e}$
VI	α-D-arabino	H	7.81	8.55	8.30	2.93	2.17	c	−13.30
VII	α-D-ribo[d]	$COCH_3$	7.74	4.36	4.15	3.97	8.32[f]	4.13[g]	−11.97

[a] Data obtained from spectra measured at 270 MHz. [b] The C-5 and C-6 protons resonating at lower field are designed H-5 and H-6, respectively, and those resonating at higher field are designed H-5' and H-6', respectively. [c] First-order coupling constants was not observed. [d] Data obtained at 500 MHz. [e] $J_{5,6\text{-}CH_3}$ = 6.20 Hz. [f] $J_{4,5a}$. [g] $J_{4,5e}$. [h] See Table III for structure.

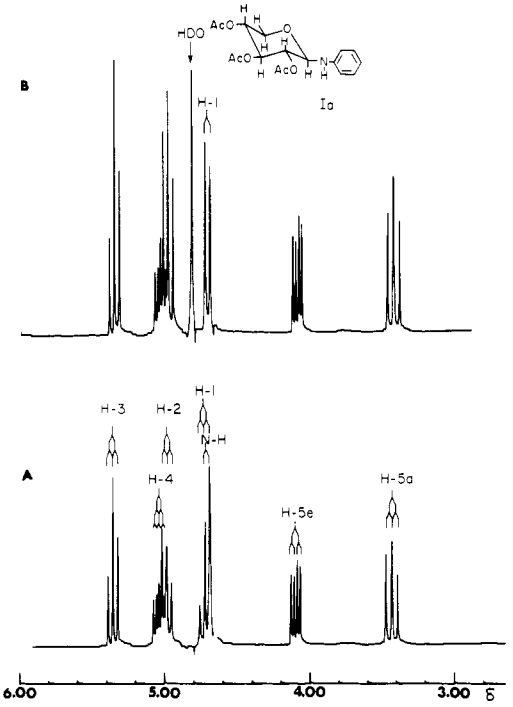

Figure 1. (A) Partial ^1H NMR spectrum of N-phenyl-2,3,4-tri-O-acetyl-β-D-xylopyranosylamine (Ia) at 270 MHz in $CDCl_3$. (B) ^1H NMR spectrum after D_2O exchange.

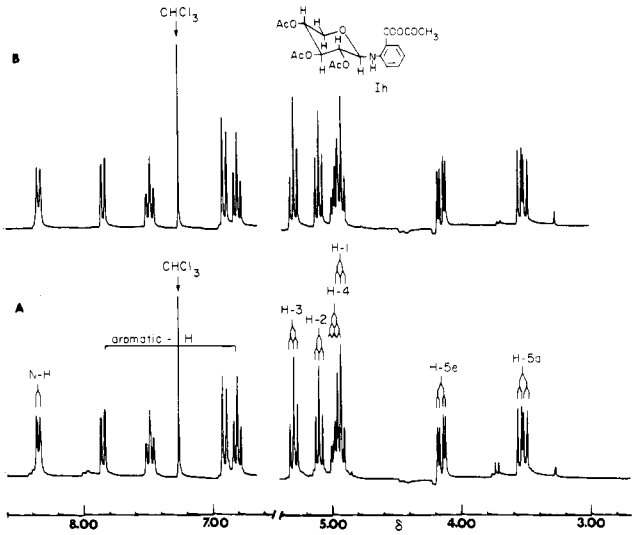

Figure 2. (A) ^1H NMR spectrum of N-[(acetoxycarbonyl)-phenyl]-2,3,4-tri-O-acetyl-β-D-xylopyranosylamine (Ih) at 270 MHz in $CDCl_3$. (B) ^1H NMR spectrum after D_2O exchange.

of the 1-NH proton downfield was 3.01 ppm. This phenomenon may be due not only to the fact that the ortho substituent in Ih was much more deshielding than that of the corresponding para derivative but also to the formation of hydrogen bonding between the o-$COOCOCH_3$ group and the 1-NH proton.[26,27] In agreement with this possibility, this NH proton could not be exchanged by deuterium oxide. Analysis of the NMR spectrum of this compound was accomplished by spin-decoupling techniques.

Tetra-O-acetyl-β-D-glucopyranosylamine (II). The NMR spectrum of II was similar to that of the D-xylopyranosylamines (Ia–h). After D_2O exchange, the 1-NH doublet of δ 5.30 disappeared and H-1, H-2, H-3, and H-4 signals were observed as triplets at δ 4.81, 5.07, 5.41, and 5.10, respectively (Table III), with large coupling constants.[4] This finding indicated that these protons were axially oriented and existed in the *C*1 (D) conformation and the β configuration; however, Holland et al.[22] have reported that the H-1, H-2, H-3, and H-4 signals of 1-thio-β-D-glucopyranose pentaacetate overlapped and could not be analyzed when chloroform-*d* was used as a solvent at 100 MHz. The H-6 and H-6' signals appeared as an eight-line pattern, typical of the A–B portion of an ABX system,[5] and the H-5 signal appeared at a higher field (δ 3.87) as an eight-line multiplet which was readily illustrated by expansion of the spectrum and appeared as the X portion of an ABXY system.

Tetra-O-acetyl-β-D-galactopyranosylamine (III). Compound III gave an NMR spectrum consistent with the anticipated *C*1 conformation. The H-1 and H-2 signals were observed as triplets with large coupling constants ($J_{1,2}$ = 8.30 Hz, $J_{2,3}$ = 9.24 Hz), indicating that H-1, H-2, and H-3 were axially oriented and existed in the *C*1 (D) conformation and the β configuration. After D_2O exchange, the H-1 triplet at δ 4.81 collapsed to a doublet, and simultaneously the 1-NH doublet at δ 5.37 disappeared. The structure of compound III was further supported by the chemical shifts of the acetoxy groups; the lowest field acetoxy group at δ 2.17 was assigned to the axial 4-acetoxy group, and the other three acetoxy groups were at a higher field at δ 2.03, 2.06, and 2.08, respectively, indicating an equatorial orientation.[4,24,25]

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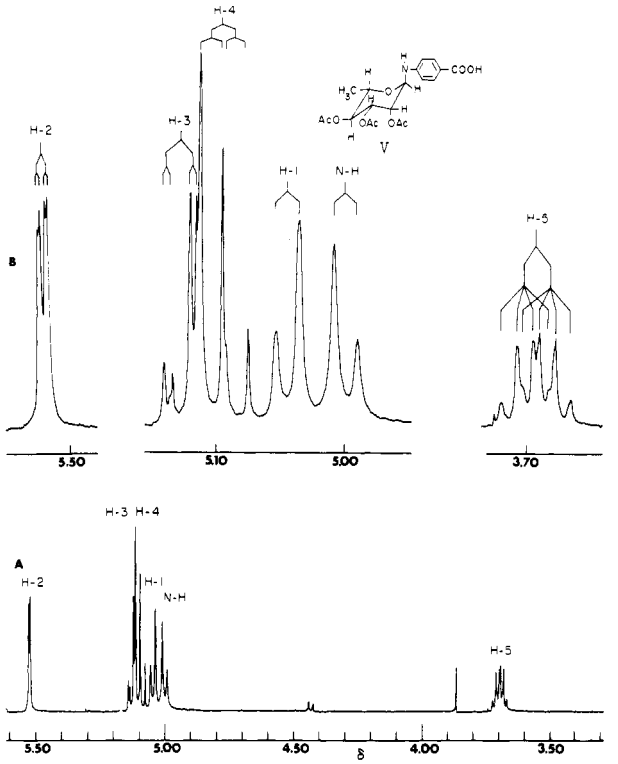

Figure 3. (A) Partial ^1H NMR spectrum of *N*-(*p*-carboxyphenyl)-2,3,4-tri-*O*-acetyl-α-L-rhamnopyranosylamine (V) at 500 MHz in $CDCl_3$. (B) Expansion of the spectrum A.

Tetra-*O*-acetyl-α-D-mannopyranosylamine (IV). The NMR spectrum of compound IV was consistent with an α-D configuration in the *C*1 conformation. Upon D_2O exchange, the doublet at δ 5.35 disappeared; this signal was assigned to 1-NH. The other broad doublet at δ 5.05 collapsed to a broad singlet and was assigned to H-1. The H-1 was considered to be in the equatorial orientation,[4] since the $J_{1e,2e}$ coupling constants were apparently too small to be separated. The quartet at δ 5.17 was assigned to H-3, which showed a small $J_{2,3}$ (3.32 Hz) and a large $J_{3,4}$ (9.97 Hz) coupling. The H-4 appeared as a triplet, indicating that H-3, H-4, and H-5 existed in an axial orientation.[4] The signals and the chemical shifts of the H-5, H-6, and H-6′ protons were similar to those of the corresponding protons in compound III. These findings all supported the *C*1 (D) conformation and α configuration. Similarly, the chemical shifts of the acetoxy groups gave further support to the assigned structure, since one acetoxy group signal appeared at relatively low field at δ 2.30 and was assigned to the axial 2-acetoxy group.[4,24,25]

Tri-*O*-acetyl-L-rhamnopyranosylamine (V). The NMR spectrum of compound V is shown in Figure 3. At 500 MHz all of these protons were resolved. After D_2O exchange, the broad doublet at δ 5.04 collapsed to a narrow doublet with a small coupling constant ($J_{1,2}$ = 0.94 Hz) which was assigned to H-1. The NH and H-1 protons appeared to be an AB system. These findings indicated that the H-1 proton existed in an equatorial orientation.[4] The doublet at δ 4.99 that disappeared was assigned to 1-NH. The large coupling constant of $J_{3,4}$ (9.64 Hz) and $J_{4,5}$ (10.10 Hz) indicated that H-3, H-4, and H-5 existed axially in the sugar ring. The eight-line signal at higher field (δ 3.69) was assigned to H-5, the A portion of an AX_3Y system, coupled with H-4 (Y) and with three protons (X_3) at C-6. All of these data, including those for the three acetoxy groups,[4,24,25] provided support for the 1*C* (L) conformation and the α configuration and excluded the *C*1 conformation which would have 3,4,5-triequatorial protons

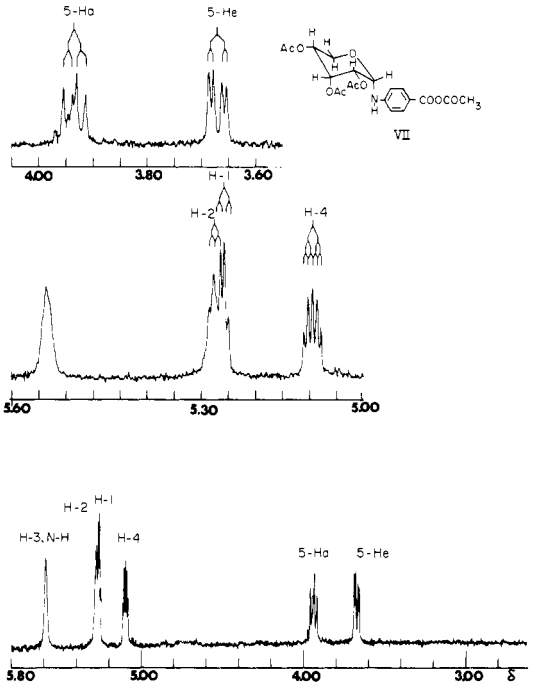

Figure 4. (A) Partial ^1H NMR spectrum of *N*-[*p*-(acetoxycarbonyl)phenyl]-2,3,4-tri-*O*-acetyl-α-D-ribopyranosylamine (VII) at 500 MHz in $CDCl_3$. (B and C) Expansions of the spectrum of A.

and $J_{3,4}$ and $J_{4,5}$ couplings of smaller magnitude.

Tri-*O*-acetyl-α-D-arabinopyranosylamine (VI). The NMR spectrum of compound VI showed a triplet with a large coupling constant at δ 4.75 ($J_{1,NH}$ = 7.81 Hz, $J_{1,2}$ = 8.55 Hz) that converted to a doublet after D_2O exchange; this was assigned to H-1. The doublet at δ 5.26 that disappeared after D_2O exchange was assigned to 1-NH. The triplet at δ 5.31 with a large coupling constant ($J_{2,3}$ = 8.30 Hz) was assigned to H-3, indicating an axial orientation of the H-1, H-2, and H-3 protons. The methylene protons (H-5, H-5′) at δ 4.05 and δ 3.79, respectively, gave a pattern recognizable as the AB portion of an ABX system. The remaining signal, a poorly resolved broad singlet at δ 5.39 was assigned to H-4. The poor resolution of this signal was assumed to be due to the small difference in the chemical shift between H-4 and H-3 (δ 5.39 for H-4 and δ 5.31 for H-3). These findings clearly support the 1*C* (D) conformation and the α configuration for compound VI. The acetoxy group signals provided further verification of the structure of VI, since one signal was observed at relatively low field (δ 2.17), indicative of the axial orientation of the 4-OAc, and the other two signals occurred at higher field (δ 2.06, 2.08), indicating equatorial orientation of the 2-OAc and 3-OAc groups.[4,24,25]

Tri-*O*-acetyl-α-D-ribopyranosylamine (VII). All of the protons of compound VII were well resolved (Figure 4), except for the signals of the H-3 and H-4 protons which overlapped, even with high-resolution NMR at 500 MHz, to form a poorly resolved broad singlet at δ 5.59. The chemical shifts of these protons were determined by the spin-decoupling technique; the methylene H-5 protons exhibited an eight-line pattern, indicating an AB portion of an ABX system. The $J_{4,5}$ coupling constant was large (8.32 Hz), indicating a trans-diaxial arrangement of the H-4 and H-5a protons. The H-1 signal appeared as a quartet (a pair of doublets) by coupling with the neighboring 1-NH and H-2 protons and had coupling constants of 7.74 ($J_{1,NH}$) and 4.36 Hz ($J_{1,2}$), respectively. These findings indicated that H-1 existed in an equatorial orientation. A triplet at

δ 5.29 was assigned to H-2. This signal was split by H-1 and H-3 protons to give a small coupling constant ($J_{2,3}$ = 4.15 Hz), indicating the existence of 1,2- and 2,3-cis orientations. The quartet of H-1 and the triplet of H-2 protons at δ 5.26 and δ 5.29, respectively, collapsed to a pair of doublets by irradiating protons H-3 and 1-NH. The H-4 proton appeared as a quintet by coupling with the neighboring axial protons at C-5 ($J_{4,5a}$ = 8.32 Hz), and the equatorial protons at C-3 and C-5 ($J_{3,4}$ = 3.97 Hz, $J_{4,5e}$ = 4.13 Hz, respectively). These observations indicated that H-4 existed in the axial orientation. The methylene H-5 protons exhibited an eight-line pattern to form the AB portion of an ABX system, and the large $J_{4,5a}$ coupling constant (8.32 Hz) indicated a trans-diaxial arrangement of H-4 and H-5a. The H-5a signal occurred at a lower field (δ 3.94) than that of the H-5e (δ 3.67), proving to be an exception to the rule that an equatorial proton resonates at a field lower than that of a chemically similar but axially oriented proton.[4] This may be the result of the deshielding effect of the axial acetoxy group at C-3. These findings support the *C*1 conformation, and exclude the 1*C* conformation, which would give a smaller $J_{4e,5a}$ coupling constant. The small splitting of the H-1 signal suggested an α-D configuration for structure VII. This was also confirmed by the acetoxy group signals, since one signal was observed at lower field (δ 2.22), indicative of the axial orientation (3-OAc), and the other two signals were observed at higher field (δ 2.10 and δ 2.13), indicating an equatorial orientation (2,4-OAc).[4,24,25]

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Supplementary Material Available: Partial ^1H NMR data for compounds Ih (Figure 5), II (Figure 6), III (Figure 7), IV (Figure 8), V (Figure 9), and VI (Figure 10) (7 pages). Ordering information is given on any current masthead page.

Evolution of Photooxidation Products upon Irradiation of Phenyl Azide in the Presence of Molecular Oxygen

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The reaction of phenylnitrene with oxygen was reinvestigated by irradiating phenyl azide (1) in O_2-saturated acetonitrile solutions. Quantum yields of the disappearance of 1 are calculated from absorption spectral changes, and primary photoproducts are determined by using high-pressure liquid chromatography. The photochemistry of the reaction products (azobenzene, azoxybenzene, nitrobenzene, and nitrosobenzene) are also examined, including measurements of quantum yields and determinations of primary photoproducts and product ratios. A reaction sequence is presented to account for the photooxidation products afforded upon irradiation of 1 in the presence of oxygen. The reaction of phenylnitrene with oxygen is an effective termination step in the autocatalytic chain decomposition of 1.

During our investigation of the photoinitiated autocatalytic chain decomposition (PACD) of phenyl azide[1] (1), azobenzene[2] (2) was the only primary photoproduct when irradiated with 254-nm light in deaerated acetonitrile (CH_3CN) solution.[3] An isosbestic point in the absorption spectra and high-pressure liquid chromatography (LC) verified the two-component system. Upon continued irradiation, the isosbestic point was destroyed as an intractable material was also formed.[4,5] Prolonged irradiation of 1 in aerated solution also afforded azoxybenzene and nitrobenzene.[1]

Abramovitch and Challand[6] have studied the photoreaction of phenyl azide with oxygen in CH_3CN and found nitrobenzene and tars as major photoproducts; trace amounts of azobenzene and aniline were also formed. Upon triplet sensitization, the amount of nitrobenzene was substantially increased; no azobenzene or aniline was formed. Direct excitation of 1 in the presence of the triplet quencher piperylene resulted in negligible amounts of nitrobenzene.[6] Five substituted phenyl azides were also studied,[7] with nitrobenzenes being formed. Corresponding azobenzenes, anilines, and azoxybenzenes were also formed. Azoxybenzene is thought to be formed via reaction of an arylnitrene with its nitrosobenzene;[6,11,12] direct oxidation

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