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HETEROCYCLIC N-GLYCOSYL DERIVATIVES—XI

SYNTHESIS AND NMR CONFORMATIONAL STUDY OF N-GLYCOSYL BENZOTRIAZOLES FROM ACETYLATED GLYCALS

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Abstract—Acid-catalyzed reaction of benzotriazole, 5,6-dimethylbenzotriazole and 5,6-dichlorobenzotriazole with di-O-acetyl-D-xylal in ethyl acetate afforded 1-(4'-O-acetyl-2',3'-dideoxy-D-*glycero*-pent-2'-enopyranosyl)benzotriazole derivatives and small amounts of 1,2,3-trideoxy-4-O-acetyl-3-(benzotriazolyl)-D-*threo*-pent-1-enopyranose derivatives. The reactions using di-O-acetyl-L-arabinal led to the formation of the corresponding 1- and 2-(3',4'-di-O-acetyl-2'-deoxy-L-*erythro*-pentopyranosyl)benzotriazole derivatives. In addition the enantiomers of the above 2',3'-unsaturated N-glycosyl compounds were also obtained. The configurations and conformations of the products obtained were determined by NMR spectroscopy.

IN A PRELIMINARY communication[1] we described the preparation of some 2',3'-unsaturated N-glycosyl benzotriazoles from 3,4-di-O-acetyl-D-xylal, a glycal with *trans* related acetoxy groups at C-3 and C-4, and 3,4-di-O-acetyl-L-arabinal in which these substituents are *cis* oriented. More recently it has been shown that those N-glycosyl derivatives[2] and the related anomeric 9-(4',6'-di-O-acetyl-2',3'-dideoxy-α- and β-D-*erythro*-hex-2'-enopyranosyl)-2,6-dichloropurine,[3] rearrange to give 3-deoxyglycal derivatives with the base moiety bonded to C-3 of the carbohydrate. Epimeric mixtures of this new type of unsaturated nucleoside analog with glycal structures were also formed in the fusion of 3,4,6-tri-O-acetyl-D-glucal with 2-methylthio-6-chloropurine[4] and 2,6-dichloropurine,[3] whilst from the reaction of 3,4-di-O-acetyl-D-xylal and 3,4-di-O-acetyl-L-arabinal with 6-chloropurine[5] in EtOAc solution, only one of the two C-3 epimeric isomers was identified.

In this paper we report additional studies on the synthesis of N-glycosyl benzotriazoles starting from acetylated glycals (D-xylal and L-arabinal). The configurations and conformations of the compounds obtained were established from analysis of their NMR spectra.

When a mixture of benzotriazole and 3,4-di-O-acetyl-D-xylal in EtOAc containing a few drops of trifluoracetic acid was heated in a sealed tube at 95–100° under continuous agitation for 24 hr, four products were isolated, namely, 1- and 2-(4'-O-acetyl-2',3'-dideoxy-β-D-*glycero*-pent-2'-enopyranosyl)benzotriazole (IIIa and IIIb), 1,2,3-trideoxy-4-O-acetyl-3-(benzotriazol-2-yl)-D-*threo*-pent-1-enopyranose (Ib), and 1,2,3-trideoxy-4-O-acetyl-3-(benzotriazol-1-yl)-D-*threo*-pent-1-enopyranose (Ia). On the

other hand the reaction of benzotriazole with 3,4-di-O-acetyl-L-arabinal was found to give compounds III'a, III'b and I'b which were shown to be the enantiomers of the above IIIa, IIIb and Ib. In addition three saturated N-glycosyl derivatives were also obtained 2-(3',4'-di-O-acetyl-2'-deoxy-β-L-*erythro*-pentopyranosyl) benzotriazole (Vb) and 1-(3',4'-di-O-acetyl-2'-deoxy-β- and α-L-*erythro*-pentopyranosyl)benzotriazole (Va and IVa).

5,6-Dimethylbenzotriazole reacted with 3,4-di-O-acetyl-D-xylal to give 11% yield of 1-(4'-O-acetyl-2',3'-dideoxy-α-D-*glycero*-pent-2'-enopyranosyl)-5, 6-dimethylbenzotriazole (IIc). When 3,4-di-O-acetyl-L-arabinal was used, four compounds were isolated, namely, the corresponding enantiomer II'c of the above N-glycosyl derivative IIc, 2-(3',4'-di-O-acetyl-2'-deoxy-β-L-*erythro*-pentopyranosyl)-5,6-dimethylbenzotriazole (Vd), and 1-(3',4'-di-O-acetyl-2'-deoxy-β- and α-L-*erythro*-pentopyranosyl)-5,6-dimethylbenzotriazole (Vc and IVc), respectively.

Reaction between 5,6-dichlorobenzotriazole and 3,4-di-O-acetyl-D-xylal gave 1-(4'-O-acetyl-2',3'-dideoxy-β-D-*glycero*-pent-2'-enopyranosyl)-5,6-dichlorobenzotri-

TABLE 1. UV ABSORPTION SPECTRA OF THE PRODUCTS OBTAINED AND RELATED 1- AND 2-ALKYLBENZOTRIAZOLES

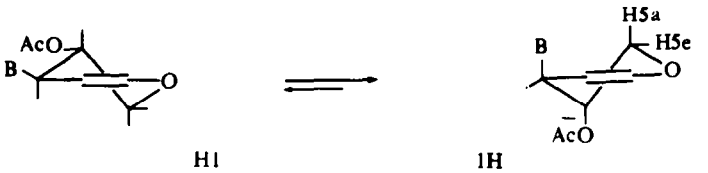
Compound	λ_{max}^{EtOH}	ε	λ_{max}^{EtOH}	ε
1-Methylbenzotriazole[13]	255	6,457	283	4,786
2-Methylbenzotriazole[13]	275	7,943		
IIIa	253·5	7,240	280	3,950
III'a	254	7,040	280	3,910
Ib	273	10,550		
I'b	273	10,700		
Ia	254	7,670	280	4,750
Vb	273	11,200		
Va	255	7,250	281	4,460
IVa	254	8,100	281	4,960
IIc	259	7,800	289	4,630
II'c	260	7,650	289	4,460
Vd	284	12,000	294	10,400
Vc	261	8,300	288	4,850
IVc	261	7,650	288	4,460

Compound	λ_{max}^{EtOH}	ε	λ_{max}^{EtOH}	ε	λ_{max}^{EtOH}	ε
1-Methyl-5,6-dichlorobenzotriazole[14]	268	4,786	272	5,012	295	4,169
2-Methyl-5,6-dichlorobenzotriazole[14]	286	7,762	293	8,913	300	6,918
IIIe	263	7,200	270	6,760	296	4,515
III'e	263·5	7,420	271	6,840	298	4,900
III'f	287	10,900	296	13,500	306	11,500
II'e	263·5	7,200	271	6,700	298	4,975
I'e	267	7,500	274	7,500	297	5,100
IVe	263	6,930	270	6,420	298	4,750
IVf	286	10,100	295	12,125	305	10,770
Ve	264	6,880	272	6,450	297	4,600
Vf	287	10,750	296	13,200	306	11,300

azole (IIIe) in moderate yield. However, when the 3,4-di-O-acetyl-L-arabinal was used, eight N-glycosyl derivatives were obtained: 1- and 2-(4′-O-acetyl-2′,3′-dideoxy-β-L-*glycero*-pent-2′-enopyranosyl)-5,6-dichlorobenzotriazole (III′e and III′f), 1-(4′-O-acetyl-2′,3′-dideoxy-α-L-*glycero*-pent-2′-enopyranosyl)-5,6-dichlorobenzotriazole (II′e), 1,2,3-trideoxy-4-O-acetyl-3(5,6-dichlorobenzotriazol-1-yl)-L-*threo*-pent-1-enopyranose (I′e), 1- and 2-(3′,4′-di-O-acetyl-2′-deoxy-α-L-*erythro*-pentopyranosyl)-5,6-dichlorobenzotriazole (IVe and IVf), and 1- and 2-(3′,4′-di-O-acetyl-2′-deoxy-β-L-*erythro*-pentopyranosyl)-5,6-dichlorobenzotriazole (Ve and Vf).

The site of glycosidation for the above products was easily determined by comparison of their UV spectra with the UV absorption data reported for 1- and 2-alkylbenzotriazoles (Table 1), and it was confirmed by the appearance of the pattern of the aromatic protons in the NMR spectra.

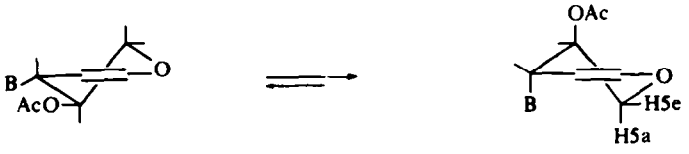
CHART 1



H1 1H

I

Ia B = benzotriazol-1-yl
Ib B = benzotriazol-2-yl



1H(L) H1(L)

I′

I′b B = benzotriazol-2-yl
I′e B = 5,6-dichlorobenzotriazol-1-yl

The configurations and conformations of both the unsaturated and saturated N-glycosyl benzotriazoles were established by NMR studies. Table 2 lists the proton magnetic parameters obtained for compounds Ib, Ia, I′b and I′e (Chart I). As the values found were closely similar to those previously reported[5] for 1,2,3-trideoxy-4-O-acetyl-3-(6-chloropurin-9-yl)-D-*threo*-pent-1-enopyranose which mainly exists in the 1H conformation, it was assumed that all these compounds take the same 1H or H1(L)*

* Through this work, H1, 1H, C1 and 1C refer to D-sugars while H1(L), 1H(L), C1(L) and 1C(L) refer to L-sugars. It must be kept in mind that the pairs H1 and 1H(L), 1H and H1(L), C1 and 1C(L), and finally 1C and C1(L) are mirror images and that the substituents in each pair will therefore have the same axial or equatorial arrangement.

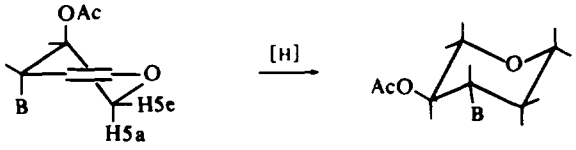
TABLE 2. NMR PARAMETERS OF 1,2,3-TRIDEOXY-4-O-ACETYL-3-(BENZOTRIAZOLYL)-THREO-PENT-1-ENOPYRANOSE DERIVATIVES CHEMICAL SHIFTS ((τ-values)

Compound	N-subst.	Solvent	Conformation (%)	H-1	H-2	H-3	H-4	H-5a	H-5e	AcO	Base (protons)
Ia	N-1	$CDCl_3$	1H (70–80%)	3·16	4·91	4·65	4·65	5·77	5·77	7·90	1·92 (1), 2·1-2·8 (3)
Ia	N-1	C_6D_6	1H (70–80%)	3·53	5·42	4·97	4·97	6·32	6·09	8·47	1·98(1) 2·40(1), 2·6–3·1 (2)
Ib and I'b	N-2	$CDCl_3$	1H and H1 (L) (70–80%)	3·22	4·88	4·51	4·51	5·76	5 64	7·90	2·12(l), 2·64 (2)
Ib and I'b	N-2	C_6D_6	1H and Hl (L) (70–80%)	3·52	5·12	4·39	4·59	6·05	5·71	8·43	2·16(2). 2·90 (2)
I'e	N-1	$CDCl_3$	Hl (L) (70–80%)	3·16	4·99	4·58	4·84	5·80	5·80	7·90	1·89 (1), 2·06 (1)

Coupling Constants (Hz)

Compound	N-subst.	Solvent	$J_{1,2}$	$J_{1,3}$	$J_{2,3}$	$J_{2,4}$	$J_{3,4}$	$J_{3,5e}$	$J_{4,5a}$	$J_{4,5e}$	$J_{5a,5e}$
Ia	N-1	C_6D_6	6·3	−1·5	4·3	1·6		1·5	2·5	4·5	−12·0
Ib and I'b	N-2	C_6D_6	6·4	−1·5	4·7	1·3		1·3	1·6	4·0	−12·3
I'e	N-1	$CDCl_3$	6·0	−1·6	3·7						

half-chair conformations. The multiplets near 6·0 τ were assigned to H-5a and H-5e,* and the corresponding values of $J_{4,5a}$ and $J_{4,5e}$ were determinated by analysis of the group of signals due to these protons, which can be treated as the AB portion of an ABX system. The H-5e signal was easily identified because of the observed long-range couplings between H-3 and H-5e ($J_{3,5e}$ = 1·3–1·5 Hz) which are in a W arrangement. The fact that the values of $J_{4,5a}$ are rather smaller than those of $J_{4,5e}$ suggests that there may exist an appreciable contribution of the H1 or 1H(L) conformations, because in these forms H-4 and H-5e are now in an axial-axial arrangement. Finally, it was observed that the upfield $CHCl_3$-C_6H_6 shift was larger for H-5a than for H-5e, a fact that we have noted in other derivatives in which the base and the H-5 protons are in a similar relationship. Additional support for the configurations at C-3 and C-4 was obtained from the NMR spectrum of VIe, a compound readily available by catalytic hydrogenation of I'e. The large value observed for $J_{3,4}$ (9·3 Hz) indicates that H-3 and H-4 are in a *trans*-diaxial arrangement.



I'e VIe

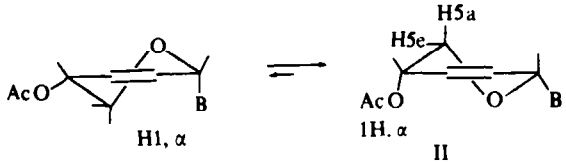
The configurations and conformations of the products included in Chart 2 were assigned on the basis of their NMR spectra, as previously illustrated.[5] The NMR spectra of compounds II'e and III'a (in $CDCl_3$ and C_6D_6) were analyzed by using the computer programs NMRIT and NMREN. A total of about 35 lines were measured for each compound, and the mean deviation between observed and calculated line frequencies was ± 0·10 Hz. The maximum errors were ± 0·01 ppm for the chemical shifts and ± 0·1 Hz for the coupling constants.

Table 3 gives the NMR parameters obtained for the above compounds. The conformations could be determined either from the magnitude of the couplings between H-4' and H-5' protons ($J_{4',5'a}$ and $J_{4',5'e}$) or from the value of the sum of both constants, when the chemical shifts for H-5'a and H-5'e protons accidentally coincided. As reference values were taken those reported by Lemieux *et al.*,[6] for the related compounds methyl 4-O-acetyl-2,3-dideoxy-β-L-*glycero*-pent-2-enopyranoside (H1(L), $J_{4,5a}$ = 3·0 Hz, $J_{4,5e}$ = 1·2 Hz) and methyl-4-O-acetyl-2,3-dideoxy-α-L-*glycero*-pent-2-enopyranoside (1H(L), $J_{4,5a}$ = 8·5 Hz, $J_{4,5e}$ = 6·0 Hz), which are considered to be conformationally homogeneous owing to the strong anomeric effect of the OMe substituent.

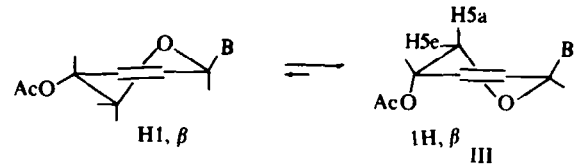
The anomeric configurations were determinated from the value of the corresponding coupling constant $J_{1',2'}$, when this can be accurately measured, which are in keeping with the values reported for analogous molecules,[3] and also with that obtained[7] from the analysis of the NMR spectra of the 6-chloro-9-(4',6',-di-O-acetyl-2',3'-dideoxy-α-

* In this paper, H-5a, and H-5e invariably refer to the more abundant conformation. It must be noted that in the alternative conformation these protons are differently oriented.

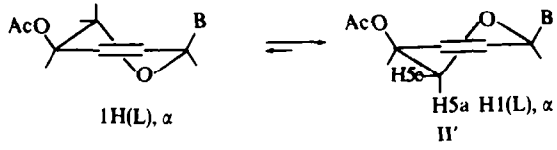
CHART 2



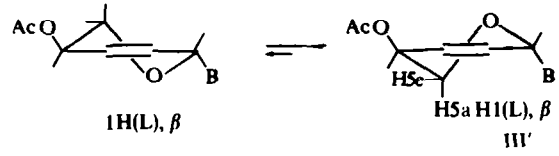
IIc B = 5,6-dimethylbenzotriazol-1-yl



IIIa B = benzotriazol-1-yl
IIIb B = benzotriazol-2-yl
IIIe B = 5,6-dichlorobenzotriazol-1-yl



II'c B = 5,6-dimethylbenzotriazol-1-yl
II'e B = 5,6-dichlorobenzotriazol-1-yl



III'a B = benzotriazol-1-yl
III'b B = benzotriazol-2-yl
III'e B = 5,6-dichlorobenzotriazol-1-yl
III'f B = 5,6-dichlorobenzotriazol-2-yl

TABLE 3. NMR PARAMETERS OF 2',3'-DIDEOXY-PENT-2'-ENOPYRANOSYL-BENZOTRIAZOLE DERIVATIVES, CHEMICAL SHIFTS (τ values)

Compound	N-subst.	Anom.	Solvent	Conformation (%)	H-1'	H-2'	H-3'	H-4'	H-5'a	H-5'e	AcO	Base (protons)
IIc and II'c	N-1	α	$CDCl_3$	1H and HI (L) (60–70%)	3·36	3·66	3·66	4·61	5·89	6·07	7·85	2·18 (1), 2·45 (1), 7·58 (6)
II'e	N-1	α	$CDCl_3$	HI (L) (60–70%)	3·27	3·77	3·55	4·64	5·87	5·99	7·78	1·85 (1), 2·00 (1)
IIIa and III'a	N-1	β	$CDCl_3$	1H and HI (L) (80–90%)	3·42	3·42	3·42	4·79	6·07	6·07	7·88	1·90 (1), 2·1–2·8 (3)
IIIa and III'a	N-1	β	C_6D_6	1H and HI (L) (80–90%)	3·92	3·80	4·08	5·14	6·39	6·39	8·35	1·90 (1), 2·4–3·1 (3)
IIIb and III'b	N-2	β	$CDCl_3$	1H and HI (L) (90–100%)	3·32	3·60	3·60	4·80	5·70	6·00	7·89	2·12 (2), 2·64 (2)
IIIe and III'e	N-1	β	$CDCl_3$	1H and HI (L) (90–100%)	3·47	3·47	3·47	4·79	6·08	6·08	7·87	1·84 (1), 2·20 (1)
III'f	N-2	β	$CDCl_3$	HI (L) (90–100%)	3·35	3·59	3·59	4·82	5·70	5·96	7·87	1·99 (2)

Coupling Constants (Hz)

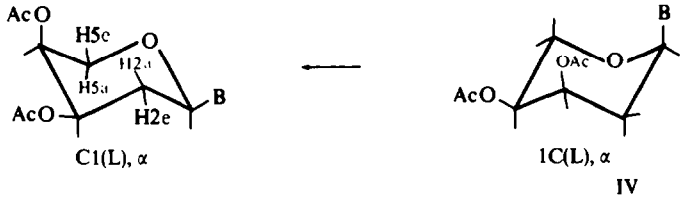
Compound	N-subst.	Anom.	Solvent	$J_{1',2'}$	$J_{1',3'}$	$J_{1',4'}$	$J_{2',3'}$	$J_{2',4'}$	$J_{3',4'}$	$J_{4',5'a}$	$J_{4',5'e}$	$J_{5'a,5'e}$
IIc and II'c	N-1	α	$CDCl_3$	1·6	−1·2	1·6	9·8	?	2·9	3·7	5·2	−12·0
II'e	N-1	α	$CDCl_3$	2·09	−2·04	1·85	10·22	−0·64	4·23	3·74	3·86	−12·16
IIIa and III'a	N-1	β	$CDCl_3$[a]							sum 4·1		
IIIa and III'a	N-1	β	C_6D_6	3·29	−1·90	0·0	10·43	−0·38	5·10	sum 4·66		?
IIIb and III'b	N-2	β	$CDCl_3$[a]							2·9	1·0	−13·5
IIIe and III'e	N-1	β	$CDCl_3$[a]							sum 4·4		
III'f	N-2	β	$CDCl_3$[a]							2·4	1·5	−13·3

[a] Values of coupling constants in this solvent could not be drawn because of nearly coincidence of H-1', H-2' and H-3' protons.

and β-D-*erythro*-hex-2'-enopyranosyl)purine ($J_{1'e,2'}$ = 3·05 Hz and $J_{1'a,2'}$ = 1·82 Hz, respectively). In addition, the magnitudes of the other coupling constants, especially $J_{1',4'}$ and $J_{3',4'}$ clearly support all the above conclusions.[3,5]

The β compounds preferently adopt the 1H or H1(L) conformations (~ 80–100%). The proportion of each conformer was evaluated from the sum of $J_{4',5'a} + J_{4',5'e}$ in conjunction with the above indicated values recorded by Lemieux[6] for the two half-chair conformations. It may be noted that for N-1 substituted β-anomers, the chemical shifts for H-5'a and H-5'e coincide. When replacing the benzotriazol-1-yl substituent by benzotriazol-2-yl a deshielding of ~ 0·4 ppm is observed for one of these protons. For the 2-deoxypyranosyl benzotriazole derivatives (see below) where the assignment

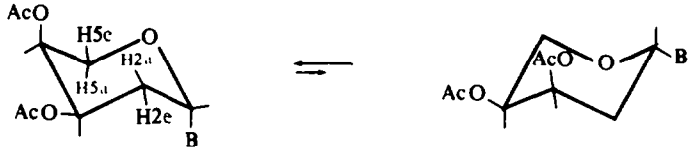
CHART 3



C1(L), α 1C(L), α

IV

IVa B = benzotriazol-1-yl
IVc B = 5,6-dimethylbenzotriazol-1-yl
IVe B = 5,6-dichlorobenzotriazol-1-yl
IVf B = 5,6-dichlorobenzotriazol-2-yl



C1(L), β 1C(L), β

V

Va B = benzotriazol-1-yl
Vb B = benzotriazol-2-yl
Vc B = 5,6-dimethylbenzotriazol-1-yl
Vd B = 5,6-dimethylbenzotriazol-2-yl
Ve B = 5,6-dichlorobenzotriazol-1-yl
Vf B = 5.6-dichlorobenzotriazol-2-yl

of H-5'a and H-5'e is unambiguous, a similar shift was observed for H-5'a. Thus, the low and high-field absorptions were assigned to H-5'a and H-5'e, respectively (Table 3). The coupling constants $J_{4',5'e}$ = 1·0–1·5 Hz and $J_{4',5'a}$ = 2·4–2·9 Hz and the values for the sum $J_{4',5'a} + J_{4',5'e}$ = 4·1–4·66 Hz found for the β-anomers are similar to those above mentioned for methyl 4-O-acetyl-2,3-dideoxy-β-L-*glycero*-pent-2-enopyranoside.[6]

The α-anomers also assume the half-chair 1H conformation(H1 (L) when derived from L-arabinal), but the alternative form exists in a higher proportion than before (30–40%). The H-5'e signal (Chart 2) was assigned to the multiplet showing the larger coupling with H-4'. This coupling is a consequence of the contribution of the Hl conformation in which the H-4' and H-5'e protons are in an *quasi*-axial-axial relationship.

TABLE 4. NMR PARAMETERS OF 2'-DEOXYPENTOPYRANOSYL-BENZOTRIAZOLE DERIVATIVES CHEMICAL SHIFTS (τ-values)

Compound	N-subst.	Anom.	Solvent	Conformation (%)	H-1'	H-2a'	H-2'e	H-3'	H-4'	H-5'a	H-5'e	AcO	Base (protons)
IVa	N-1	α	$CDCl_3$	Cl (L) (90–100%)	3·87	6·90	7·58	4·70		6·05	5·79	7·78, 7·94	1·91(1). 2·1–2·8(3).
IVa	N-1	α	C_6D_6	Cl (L) (90–100%)	4·43	6·98	7·99	4·99	4·83	6·76	6·21	8·23, 8·26	2·01 (1), 2·47(1). 2·6–3·2(2)
IVc	N-1	α	$CDCl_3$	Cl (L) (90·100%)	3·90	6·97	?	4·68		6·06	5·78	7·76, 7·94	2·19(1). 2 50 (1) 7·58(6)
IVe	N-1	α	$CDCl_3$	Cl (L) (90–100%)	3·84	?	?	4·67		6·05	5·75	7,75, 7·94	1·82(1). 2·06 (1)
IVf	N-2	α	$CDCl_3$	Cl (L) (90–100%)	3·91	6·91	7·66	4·68		5·95	5·70	7·82, 7·98	1·96(2)
Va	N-1	β	$CDCl_3$	Cl (L) (50–60%)	3·60	7·38	7·03	4·20	4·74	6·33	6·08	7·88, 7·88	1·90 (1) 2·1–2·8 (3)
Va	N-1	β	C_6D_6	Cl (L) (50–60%)	4·13	7·65	7·27	4·15	4·84	6·88	6·44	8·21, 8·22	2·03 (1) 2·5–3·2 (3)
Vb	N-2	β	$CDCl_3$	Cl (L) (50–60%)	3·54	7·40	7·22	4·09	4·70	6·02		7·86, 7·90	2·11(2). 2·60 (2)
Vc	N-1	β	$CDCl_3$	Cl (L) (50–60%)	3·66	7·40	7·02	4·17	4·74	6·32	6·05	7·87, 7·87	2·18(1). 2·55 (1). 7·58 (6)
Vd	N-2	β	$CDCl_3$	Cl (L) (50–60%)	3·56	7·45	7·20	4·08	4·70	6·05		7·87, 7·90	2·39 (2). 7·62 (6)
Ve	N-1	β	$CDCl_3$	Cl (L) (50–60%)	3·65	7·30	7·04	4·28	4·77	6·33	6·03	7·88, 7·88	1·87(1). 2·15 (1)
Vf	N-2	β	$CDCl_3$	Cl (L) (50–60%)	3·54	7·38	7·18	4·15	4·70	6·03		7·88, 7·92	1·92(2)

Coupling Constants (Hz)

Compound	N-subst.	Anom.	Solvent	$J_{1',2'a}$	$J_{1',2'e}$	$J_{2'a,2'e}$	$J_{2'a,3'}$	$J_{2'e,3'}$	$J_{3',4'}$	$J_{4',5'a}$	$J_{4',5'e}$	$J_{5'a,5'e}$
IVa	N-1	α	$CDCl_3$	10·5	2·8					1·3	2·3	−13·4
IVa	N-1	α	C_6D_6	10·6	2·8	−12·7	11·7	4·9	3·1	1·3	2·5	−13·2
IVc	N-1	α	$CDCl_3$	10·9	2·9					1·8	2·6	−12·9
IVe	N-1	α	$CDCl_3$	10·2	3·3					1·5	2·6	−13·3
IVf	N-2	α	$CDCl_3$	10·7	2·8					1·6	2·5	−13·6
Va	N-1	β	$CDCl_3$	4·7	4·7	−13·7	8·6	4·7	3·2	2·9	5·9	−12·4
Va	N-1	β	C_6D_6	4·5	4·5	−13·7	9·4	4·6	3·0	2·7	5·2	−12·6
Vb	N-2	β	$CDCl_3$	4·6	4·6	−13·8	8·9	4·8	3·3	sum 8·2		
Vc	N-1	β	$CDCl_3$	5·0	5·0		8·8	4·4	3·4	3·1	6·2	−12·4
Vd	N-2	β	$CDCl_3$	4·6	4·6		8·4	5·2	3·2	sum 8·5		
Ve	N-1	β	$CDCl_3$	4·6	4·6	−13·4	8·3	4·4	3·1	2·9	6·2	−12·7
Vf	N-2	β	$CDCl_3$	4·7	4·7		8·8	5·4	3·4	sum 7·8		

The fact that both anomers exist predominantly in the same conformation suggests that this is probably due to the allylic effect[8] which renders the H-4′ acetoxy group into a *quasi*-axial rather than a *quasi*-equational orientation.

Table 4 lists the NMR parameters obtained for the 2-deoxypyranosyl benzotriazole derivatives formed when 3,4-di-O-acetyl-L-arabinal was used. In general, these values were obtained by first-order analysis; the H-4′, H-5′a and H-5′e signals constitute an ABX system, where X is H-4′. The NMR spectra of the α-anomers (Chart 3) are entirely similar to that of 6-chloro-9-(3′,4′-di-O-acetyl-2′-deoxy-α-L-*erythro*-pentopyranosyl)purine[5] which exists predominantly in the Cl (L) conformation. Consequently, the former compounds must also adopt the same chair conformation. The values of $J_{1',2'a}$, $J_{1',2'e}$, $J_{4',5'a}$, $J_{4',5'e}$ and also $J_{5'a,5'e}$[9–12] indicate the Cl(L) form as the favoured conformation (~100%). This is not surprising since the 1C(L) conformation must be expected to be much less stable relative to the Cl(L), as a consequence of the non-bonded interaction between the base and the acetoxy group at C-3′. From the values observed for the coupling constants between H-4′ and the two H-5′ protons (2·3–2·6 and 1·3–1·8 Hz) it was not possible to assign the H-5′a and H-5′e signals unambiguously. However, by comparing the $CHCl_3$–C_6H_6 shifts with those observed[7] in the compounds resulting from the catalytic hydrogenation of the 2′,3′-unsaturated N-glycosyl benzotriazole derivatives, for which an unambiguous assignment was possible on the basis of the $J_{4',5'}$ couplings, the signals at 5·95–6·06 τ and 5·70–5·79 τ were assigned to H-5′a (J = 1·3–1·8 Hz) and H-5′e (J = 2·3–2·6 Hz), respectively. It should be noted that $J_{e,e} > J_{e,a}$. This was also found to be the case for the β-D-arabinopyranose tetra-acetate[13] which exhibited a $J_{4e,5e}$ value larger than $J_{4e,5a}$ ($J_{e,e}$ = 1·5 Hz and $J_{e,a}$ = 1·2 Hz). On the other hand, the fact that the reported $J_{e,e}$ value is somewhat smaller than those observed for our compounds, suggests that in these cases there may exist a small contribution (~10%) from the less favoured 1C (L) conformation.

As for the conformation of the β-anomers, their NMR spectra represent a time average of the two chair conformations. This conclusion was mainly drawn from the values of coupling constants $J_{4',5'a}$ and $J_{4',5'e}$ (Table 4) which appeared as intermediate between the values reported by Horton and Durette[15] as representative of the two conformations (Cl(L): $J_{4e,5e}$ = 1·5 Hz and $J_{4e,5a}$ = 1·2 Hz; 1C(L): $J_{4a,5e}$ = 5·4 Hz and $J_{4a,5a}$ = 11·0 Hz). The appearance of the anomeric proton signal as a triplet showing $J_{1',2'a}$ = 4·5–5·0 Hz and $J_{1',2'e}$ = 4·5–5·0 Hz supports the above conclusion, as it will be shown in a forthcoming paper[7] in which we have studied a series of N-glycosyl compounds prepared from 3,4,6-tri-O-acetyl-D-galactal. The fact that these β-anomers exist in the Cl(L) conformation in equilibrium with the 1C(L) form is in contrast[5] to 6-chloro-9-(3′,4′-di-O-acetyl-2′-deoxy-β-L-*erythro*-pentopyranosyl)purine, for which it was shown to exist predominantly in the 1C(L) conformation.

EXPERIMENTAL

M.ps are uncorrected. NMR spectra were recorded on a Perkin–Elmer R-10 spectrometer using TMS as the internal standard. UV absorption spectra were obtained with a Perkin–Elmer 350 spectrophotometer. Optical rotations were determined on a Perkin–Elmer 141 polarimeter. Analytical TLC was performed with silica gel GF_{254} (Merck). Thick-layer chromatography (20 × 20 cm and 2 mm thickness) was performed with silica gel PF_{254} (Merck). Spots were visualized with UV light of 254 mμ.

Reaction of di-O-acetyl-glycals and benzotriazoles. The following general procedure was essentially used in all cases: a equimolecular mixture of the acetylated glycal and the benzotriazole in 50 ml of pure EtOAc with a few drops of trifluoroacetic acid was heated in a sealed tube with continuous agitation at 100–110° for 24 hr. After this time the cooled solution was filtered and the filtrate washed with water and dried (Na_2SO_4). The EtOAc was evaporated leaving a thick tan-coloured syrup which was left overnight *in vacuo* over P_2O_5 and KOH. This crude product was treated as specified in each case.

3,4-*Di*-O-*acetyl*-D-*xylal and benzotriazole.* Treatment of the crude reaction product obtained from 0·02 mole of glycal and 0·02 mole of benzotriazole with C_6H_6-light petroleum gave 1·03 g of IIIa (see below). The residue obtained by evaporation of solvent was dissolved in EtOAc and applied to 22 prep. TLC plates. The plates were developed 5 times in a mixture of EtOAc-light petroleum 1:2, resulting in the separation of 5 major bands. In all the cases products were extracted with EtOAc.

1,2,3-*Trideoxy*-4-O-*acetyl*-3-(*benzotriazol*-2-*yl*)-D-threo*pent*-1-*enopyranose* (Ib). The faster moving band afforded a syrup which was rechromatographed by prep. TLC (EtOAc-C_6H_6 1:4) to give 0·2 g of a solid, m.p. 76–77° (from EtOAc-light petroleum): $[\alpha]_D$ − 351·8° (*c* 2·5, $CHCl_3$). (Found: C, 60·29; H, 5·15; N, 16·18. $C_{13}H_{13}N_3O_3$ requires: C, 60·23; H, 5·02; N, 16·21%).

2-(4′-O-*Acetyl*-2′,3′-*dideoxy*-β-D-glycero-*pent*-2′-*enopyranosyl*) *benzotriazole* (IIIb). The following band gave a small amount of compound identified by NMR spectroscopy as IIIb.

1,2,3-*Trideoxy*-4-O-*acetyl*-3-(*benzotriazol*-1-*yl*)-D-threo-*pent*-1-*enopyranose* (Ia) The next band gave a syrup which was further purified by TLC using EtOAc-C_6H_6 1:4 as developer system giving 0·07 g of a solid, m.p. 119–120°: $[\alpha]_D$ − 216° (*c* 0·5, $CHCl_3$). (Found: C, 60·54; H, 5·16; N, 16·05. $C_{13}H_{13}N_3O_2$ requires: C, 60·23; H, 5·02; N, 16·21%).

1-(4′-O-*Acetyl*-2′,3′-*dideoxy*-β-D-glycero-*pent*-2′-*enopyranosyl*)*benzotriazole* (IIIa). The next band gave 1·6 g of white solid, m.p. 144–145° (from EtOAc-light petroleum); $[\alpha]_D$ + 120·7° (*c* 1, $CHCl_3$). This product was shown to be identical with the above previous isolated sample. (Found: C, 60·45; H, 4·92; N, 16·16. $C_{13}H_{13}N_3O_3$ requires: C, 60·23; H, 5·02; N, 16·21%).

Benzotriazole. The slower moving band afforded 0·43 g of banzotriazole.

3,4-*Di*-O-*acetyl*-D-*xylal and* 5,6-*dimethylbenzotriazole.* The glycal (0·01 mole) and 5,6-dimethylbenzotriazole (0·01 mole) were heated for 15 hr under conditions indicated above.

1-(4′-O-*Acetyl*-2′, 3′-*dideoxy*-α-D-glycero-*pent*-2′-*enopyranosyl*)-5,6-*dimethylbenzotriazole* (IIc). The crude reaction product was dissolved in C_6H_6 and the insoluble 5,6-dimethylbenzotriazole was filtered off. The filtrate was treated with light petroleum to give a chromatographically homogeneous solid. Recrystallization of this material from EtOAc-light petroleum gave IIc, m.p. 147–148°; $[\alpha]_D$ + 22·6° (*c* 1, $CHCl_3$); yield, 11%. (Found: C, 62·56; H, 5·86; N, 14·96. $C_{15}H_{17}N_3O_3$ requires: C, 62·71; H, 5·92; N, 14·63%).

3,4-*Di*-O-*acetyl*-D-*xylal and* 5,6-*dichlorobenzotriazole.* The glycal (0·02 mole) and 5,6-dichlorobenzotriazole (0·02 mole) were reacted following the above general procedure.

1-(4′-O-*Acetyl*-2′,3′-*dideoxy*-β-D-glycero-*pent*-2′-*enopyranosyl*)-5,6-*dichlorobenzotriazole* (IIIe). The crude residue was treated with warm C_6H_6. Precipitated 5,6-dichlorobenzotriazole was removed and the filtrate evaporated to dryness. This procedure was repeated 3 times resulting in the separation of the 5,6-dichlorobenzotriazole. The residue was dissolved in C_6H_6 and the soln was treated with light petroleum to give a solid. Recrystallization from C_6H_6 afforded IIIe, m.p. 184–185°; $[\alpha]_D$ + 22·4° (*c* 1, $CHCl_3$); yield, 16%. (Found: C, 47·82; H, 3·51; N, 12·96; Cl, 21·54. $C_{13}H_{11}Cl_2N_3O_3$ requires: C, 47·56; H, 3·35; N, 12·80; Cl, 21·64%).

3,4-*Di*-O-*acetyl*-L-*arabinal and benzotriazole.* A mixture of glycal (0·02 mole) and benzotriazole (0·02 mole) was heated for 40 hr as in the preceding cases. The crude thick syrup (6·73 g) was separated into 6 fractions by prep. TLC (30 plates) after 7 consecutive developments using EtOAc-light petroleum 1:1.

1,2,3-*Trideoxy*-4-O-*acetyl*-3-(*benzotriazol*-2-*yl*)-L-thro*epent*-1-*enopyranose* (I′b). The faster moving band gave a product which was further purified by thick-layer chromatography (EtOAc-C_6H_6 1:3) giving 0·09 g (1·6%) of solid I′b, m.p. 76–77°: $[\alpha]_D$ + 348·4° (*c* 1, $CHCl_3$). (Found: C, 60·35; H, 5·09; N, 16·26. $C_{13}H_{13}N_3O_3$ requires: C, 60·23; H, 5·02; N, 16·21%).

2-(4′-O-*Acetyl*-2′,3′-*dideoxy*-β-L-glycero-*pent*-2′-*enopyranosyl*)*benzotriazole* (III′b). The next band afforded a small amount of chromatographically homogeneous compound which was characterized as III′b through its NMR spectrum.

2-(3′,4′-*Di*-O-*acetyl*-2′-*deoxy*-β-L-erythro-*pentopyranosyl*)-*benzotriazole* (Vb). The solid obtained from the following band was recrystallized from EtOAc-light petroleum to yield 0·47 g (7·5%) of Vb, m.p. 270°:

$[\alpha]_D$ + 96·6° (*c* 1, $CHCl_3$). (Found: C, 56·19; H, 5·32; N, 13·06. $C_{15}H_{17}N_3O_5$ requires: C, 56·42; H, 5·32; N, 13·16%).

1-(4′-O-*Acetyl*-2′,3′-*dideoxy*-β-L-glycero-*pent*-2′-*enopyranosyl*)-*benzotriazole* (III′a). The fourth band gave 1·2 g (23%) of III′a, m.p. 144–145° (from EtOAc-light petroleum); $[\alpha]_D$ − 122·4° (*c* 0·8, $CHCl_3$). (Found: C, 60·04; H, 4·97; N, 16·14. $C_{13}H_{13}N_3O_3$ requires: C, 60·23; H, 5·02; N, 16·21%).

1-(3′,4′-*Di*-O-*acetyl*-2′-*deoxy*-β-L-erythro-*pentopyranosyl*)-*benzotriazole* (Va). The following band afforded a mixture of two products which were separated by thick-layer chromatography using EtOAc-C_6H_6 1:3 as developer. The slower moving band gave benzotriazole. The faster moving band gave Va, which was further purified by prep. TLC using EtOAc-light petroleum 1:2, m.p. 125–126° $[\alpha]_D$ + 118·2° (*c* 1, $CHCl_3$); yield, 9%. (Found: C, 56·60; H, 5·47; N, 13·16. $C_{15}H_{17}N_3O_5$ requires: C, 56·42; H, 5·32; N, 13·16%).

1-(3′,4′-*Di*-O-*acetyl*-2′-deoxy-α-L-erythro-*pentopyranosyl*)*benzotriazole* (IVa). The slower moving fraction was rechromatographed using EtOAc-C_6H_6 1:3 and EtOAc-light petroleum 1:2 to give IVa as a chromatographically homogeneous syrup, $[\alpha]_D$ − 16·7° (*c* 0·75, $CHCl_3$); yield 0·4 g (6.5%). (Found: C, 56·21; H, 5·42; N, 12·93. $C_{15}H_{17}N_3O_5$ requires: C, 56·42; H, 5·32; N, 13·16%).

3,4-*Di*-O-*acetyl*-L-*arabinal and* 5,6-*dimethylbenzotriazole*. The reaction was accomplished as for the preceding cases starting from a equimolecular mixture of glycal (0·02 mole) and the benzotriazole derivative (0·02 mole). After heating for 24 hr, 3,4-di-O-acetyl-L-arabinal (3 g, 0·015 mole) was added and the mixture was heated for 6 hr. The crude reaction product (10 g) was dissolved in $CHCl_3$ and applied to 30 prep TLC plates. The plates were developed 10 times in $CHCl_3$ resulting in the separation of 5 fractions.

2-(3′,4′-*Di*-O-*acetyl*-2′-*deoxy*-β-L-erythro-*pentopyranosyl*)-5,6-*dimethylbenzotriazole* (Vd). The product obtained from the faster moving band was crystallized from EtOAc-light petroleum to give 0·42 g (6%) of Vd, m.p. 172–173°; $[\alpha]_D$ + 87·4° (*c* 0·6, $CHCl_3$). (Found: C, 58·49; H, 5·75; N, 12·19. $C_{17}H_{21}N_3O_5$ requires: C, 58·79; H, 6·05; N, 12·10%).

1-(4′-O-*Acetyl*-2′,3′,*dideoxy*-α-L-glycero-*pent*-2′-*enopyranosyl*)-5,6-*dimethylbenzotriazole* (II′c). The second band gave 0·66 g of II′c which crystallized from EtOAc-light petroleum, m.p. 147–148°; $[\alpha]_D$ − 24·4° (*c* 0·5, $CHCl_3$). (Found: C, 62·89; H, 5·64; N, 14·70. $C_{15}H_{17}N_3O_3$ requires: C, 62·71; H, 5·92; N, 14·63%).

1-(3′,4′-*Di*-O-*acetyl*-2′-*deoxy*-β-L-erythro-*pentopyranosyl*)-5,6-*dimethylbenzotriazole* (Vc). The product obtained from the third band (0·54 g) crystallized from EtOAc-light petroleum to give pure Vc, m.p. 112–113°; $[\alpha]_D$ + 120·6° (*c* 1, $CHCl_3$). (Found: C, 59·00; H, 6·26; N, 12·14. $C_{17}H_{21}N_3O_5$ requires: C, 58·79; H, 6·05; N, 12·10%).

1-(3′,4′-*Di*-O-*acetyl*-2′-*deoxy*-α-L-erythro-*pentopyranosyl*)-5,6-*dimethylbenzotriazole* (IVc). The following band afforded 0·49 g of a solid compound. One crystallization from EtOAc-light petroleum yielded pure IVc, m.p. 113–114°; $[\alpha]_D$ − 32·5° (*c* 1, $CHCl_3$). (Found: C, 58·92; H, 6·34; N, 12·22. $C_{17}H_{21}N_3O_5$ requires: C, 58·79; H, 6·05; N, 12·10%). Finally, from the slower moving band 5,6-dimethylbenzotriazole was isolated.

3,4-*Di*-O-*acetyl*-L-*arabinal and* 5,6-*dichlorobenzotriazole*. The crude product (8·3 g) obtained from reacting the glycal (0·02 mole) and 5,6-dichlorobenzotriazole (0·03 mole) for 40 hr at 95° was dissolved in a small amount of EtOAc and the solution applied to 35 prep. TLC plates. After 15 consecutive developments using ether-light petroleum 1:3, 6 fractions were separated.

2-(4′-O-*Acetyl*-2′,3′-*dideoxy*-β-L-glycero-*pent*-2′-*enopyranosyl*)-5,6-*dichlorobenzotriazole* (III′f). The faster moving band afforded a solid compound which was crystallized from EtOAc-light petroleum to give pure III′f (0·23 g), m.p. 164–165°; $[\alpha]_D$ − 281·9° (*c* 0·5, $CHCl_3$). (Found: C, 47·34; H, 3·39; N, 12·94; Cl, 21·68. $C_{13}H_{11}Cl_2N_3O_3$ requires: C, 47·56; H, 3·35; N, 12·80; Cl, 21·64%).

1,2,3-*Trideoxy*-4-O-*acetyl*-3-(5,6-*dichlorobenzotriazol*-1-*yl*)-L-threo-*pent*-1-*enopyranose* (I′e). The product obtained from the second band was further purified by prep. TLC using $CHCl_3$ as the developer to give 0·4 g of I′e as a chromatographically homogeneous syrup, $[\alpha]_D$ + 167·3° (*c* 1·2, $CHCl_3$). (Found: C, 47·77; H, 3·53; N, 13·06; Cl, 21·30. $C_{13}H_{11}Cl_2N_3O_3$ requires: C, 47·56; H, 3·35; N, 12·80; Cl, 21·64%).

2-(3′,4′-*Di*-O-*acetyl*-2′-*deoxy*-β-L-erythro-*pentopyranosyl*)-5,6-*dichlorobenzotriazole* (Vf) *and* 1-(4′-O-*acetyl*-2′,3′-*dideoxy*-β-L-glycero-*pent*-2′-*enopyranosyl*)-5,6-*dichlorobenzotriazole* (III′e). The third band afforded 2·2 g of a mixture of two compounds, separated by prep. TLC after 10 consecutive developments with $CHCl_3$. The product obtained from the faster moving band was crystallized from EtOAc-light petroleum to yield 0·42 g of Vf, m.p. 201–202°; $[\alpha]_D$ + 100° (*c* 0·75, $CHCl_3$). (Found: C, 46·14; H, 3·85; N, 10·89; Cl, 18·15. $C_{15}H_{15}Cl_2N_3O_5$ requires: C, 46·38; H, 3·86; N, 10·82; Cl, 18·30%). The slower moving band yielded 1·2 g of III′e, m.p. 184–185° (from EtOAc-light petroleum); $[\alpha]_D$ − 25·8° (*c* 1, $CHCl_3$). (Found:

C, 47·53; H, 3·31; N, 12·98; Cl, 21·38. $C_{13}H_{11}Cl_2N_3O_3$ requires: C, 47·56; H, 3·35; N, 12·80; Cl, 21·64%).

1-(4′-O-*Acetyl*-2′,3′-*dideoxy*-α-L-glycero-*pent*-2′*enopyranosyl*)-5,6-*dichlorobenzotriazole* (II′e). The resultant crude product obtained from the fourth band was purified by prep. TLC with $CHCl_3$ as developer to give II′e, m.p. 117–118° (from EtOAc-light petroleum); $[\alpha]_D$ + 9° (*c* 0·5, $CHCl_3$); yield, 0·82 g. (Found: C, 47·30; H, 3·33; N, 12·92; Cl, 21·67. $C_{13}H_{11}Cl_2N_3O_3$ requires: C, 47·56; H, 3·35; N, 12·80; Cl, 21·64%).

1-(3′,4′-*Di*-O-*acetyl*-2′-*deoxy*-β-L-erythro-*pentopyranosyl*)-5,6-*dichlorobenzotriazole* (Ve) and 2-(3′,4′-*di*-O-*acetyl*-2′-deoxy-α-L-erythro-*pentopyranosyl*)-5,6-*dichlorobenzotriazole* (IVf). The product obtained from the next band was shown to be a mixture of two anomeric N-glycosyl derivatives, and was resolved by prep. TLC, after several developments using ether-$CHCl_3$ 1:3. The faster moving band gave 0·5 g of Ve as a chromatographically homogeneous syrup, $[\alpha]_D$ + 112·5° (*c* 0·5, $CHCl_3$). (Found: C, 46·24; H, 4·05; N, 10·59; Cl, 18·18. $C_{15}H_{15}Cl_2N_3O_5$ requires: C, 46·38; H, 3·86; N, 10·82; Cl, 18·30%). The slower moving band afforded 0·18 g of IVf, m.p. 106–107° (from EtOAc-light petroleum); $[\alpha]_D$ − 6·7° (*c* 0·5, $CHCl_3$). (Found: C, 46·65; H, 3·99; N, 10·89. $C_{15}H_{15}Cl_2N_3O_5$ requires: C, 46·38; H, 3·86; N, 10·82%).

1-(3′,4′-*Di*-O-*acetyl*-2′-*deoxy*-α-L-erythro-*pentopyranosyl*)-5,6-*dichlorobenzotriazole* (IVe). Finally, from the slower moving band a crystalline product (0·3 g) was obtained. Recrystallization from EtOAc-light petroleum gave pure IVe, m.p. 167–168°; $[\alpha]_D$ − 58·7° (*c* 1, $CHCl_3$). (Found: C, 46·24; H, 3·90; N, 10·93; Cl, 18·63; $C_{15}H_{15}Cl_2N_3O_5$ requires: C, 46·38; H, 3·86; N, 10·82; Cl, 18·30%).

1,2,3-*Trideoxy*-4-O-*acetyl*-3-(5,6-*dichlorobenzotriazol*-1-*yl*)-L-threo-*pentopyranose* (VIe). A soln of 0·145 g of I′e in 10 ml EtOAc (Merck) was hydrogenated under 3 at in the presence of PtO_2. After removal of catalyst and solvent the residue was purified by prep. TLC with ether as developer, to give 0·11 g of VIe as the only product, m.p. 148–149° (from EtOAc-light petroleum); $[\alpha]_D$ − 69·6° (*c* 1, $CHCl_3$). (Found: C, 47·36; H, 3·98; N, 12·83. $C_{13}H_{13}Cl_2N_3O_3$ requires: C, 47·27; H, 3·94; N, 12·72%).

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