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Acid-catalyzed dehydrative cyclization of 4-(D-*galacto*-pentitol-1-yl)-2-phenyl-2*H*-1,2,3-triazole. Synthesis and anomeric configuration of D-*lyxo*-*C*-nucleoside analogs

Mohammed A.E. Sallam,[a],* Somaya M.E. Abdel Megid,[a] Leroy B. Townsend[b]

[a] *Department of Chemistry, Faculty of Science, Alexandria University, Alexandria, Egypt*
[b] *Department of Medicinal Chemistry, School of Pharmacy, University of Michigan, Ann Arbor, MI 48109, USA*

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Abstract

Dehydration of 4-(D-*galacto*-pentitol-1-yl)-2-phenyl-2*H*-1,2,3-triazole with 20% methanolic sulfuric acid afforded the anomeric pairs of nucleosides, 4-(α-D-lyxopyranosyl)-2-phenyl-2*H*-1,2,3-triazole (major component) and its β-anomer, as well as 4-(α-D-lyxofuranosyl)-2*H*-1,2,3-triazole and its β-anomer. The four anomeric *C*-nucleosides were separated by chromatography, and their structure and anomeric configuration were determined by periodate oxidation, acylation, and NMR spectroscopy as well as mass spectrometry. The anomeric assignment from optical rotation was not in agreement with final structure assignment and represented a violation of the Hudson isorotation rules. NOE studies and X-ray diffraction measurements confirmed the anomeric configuration. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: 2-Phenyl-2*H*-1,2,3-triazoles; α- and β-D-Lyxopyranosyl-α- and β-D-lyxofuranosyl-*C*-nucleosides; Anomeric configuration

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1. Introduction

We have been interested lately in the synthesis of heterocyclic *C*-nucleoside analogs by the dehydrative cyclization of heterocyclic polyhydroxyalkyl analogs. Acid-catalyzed dehydration of tetritol-1-yl heterocyclic analogs having four carbon atoms in the polyhydroxyalkyl chain[1–8] is stereoselective with the formation of a preponderant isomer having a trans arrangement of the base moiety and a 2′-OH group. The change of the base moiety has no effect on the stereoselectivity of this process.[2,8]

The dehydrative cyclization of pentitol-1-yl heterocyclic analogs having five carbon atoms in the polyhydroxyalkyl chain is less stereoselective. Acid-catalyzed dehydration of epimeric 4-D-*gluco*- and 4-D-*manno*-hept-2-ulose phenylosazones gave a mixture of pyranosyl and furanosyl analogs.[9] The products were isolated by chromatography, and their structure and anomeric configuration were determined by spectral measurements. In a previous report,[10] the acid-catalyzed dehydration of D-*galacto*-2-heptulose phenylosazone and subsequent reflux with copper sulfate afforded the anomeric 4-(α- and β-D-lyxopyranosyl)-2-

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* Corresponding author. Tel.: + 203-481-2110; fax: + 203-391-1794.

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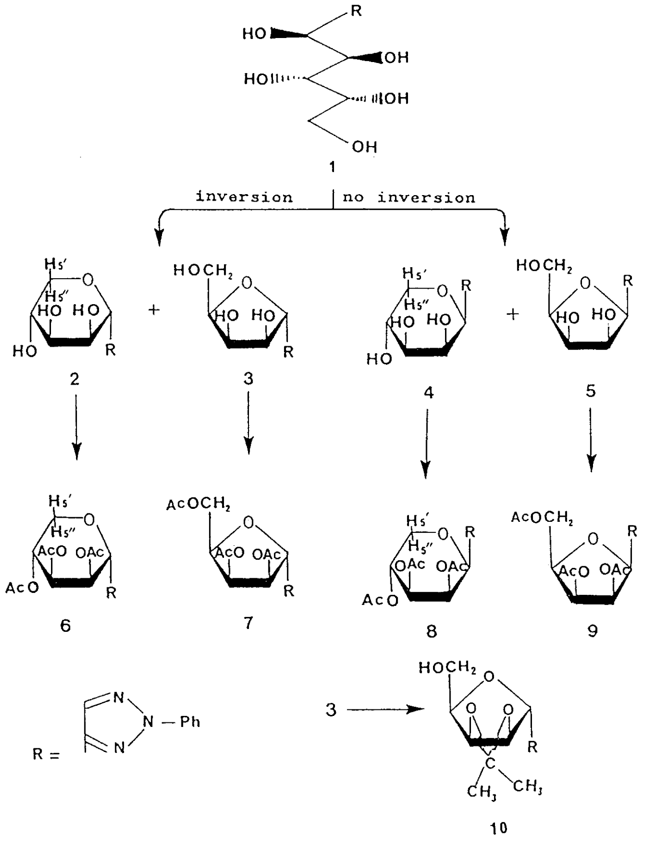
phenyl-2*H*-1,2,3-triazole-*C*-nucleosides (**2** and **4**) which were separated from the reaction mixture by fractional recrystallization in lower yield. Their structure and anomeric configuration were erroneously assigned as anomeric lyxofuranosides.

2. Results and discussion

In the present work, 4-(D-*galacto*-pentitol-1-yl)-2-phenyl-2*H*-1,2,3-triazole (**1**), which is more stable in acid medium than the precursor phenylosazone — a property that makes it more suitable for dehydrative cyclization — was subjected to acid-catalyzed dehydrative cyclization, giving better yield (40% total yield) of anomeric pyranosyl and furanosyl D-*lyxo*-*C*-nucleoside analogs. The dehydrative cyclization of **1** was effected by refluxing with 20% methanolic sulfuric acid solution with monitoring the reaction by TLC. The 4-(α-D-lyxopyranosyl)-2-phenyl-2*H*-1,2,3-triazole (**2**) (Scheme 1) was obtained as the predominant isomer that crystallized from the syrupy mixture and was partially separated by filtration. The mother liquor was chromatographed on an ion-exchange resin (OH^-) form, with gradient elution with aqueous methanol. The pyranosyl anomer **2**, followed by 4-(β-D-lyxopyranosyl)-2-phenyl-2*H*-1,2,3-triazole (**4**), were eluted first from the column with 60% aqueous methanol. These were followed by the furanosyl anomeric pair, 4-(α-D-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole (**3**), and its anomer, 4-(β-D-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole (**5**). The byproduct 4-(5′-*O*-methyl-α-D-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole (**11**) was finally eluted from the column with 90% aqueous methanol.



Scheme 1.

Periodate oxidation of **2** and **4** consumed two moles of oxidant in accord with the pyranosyl ring structure. The ^{1}H NMR spectrum of **2** (Table 1) showed a triplet at δ 4.99 of two protons intensity corresponding to two overlapped hydroxyls and a doublet at δ 4.69 that disappeared by deuteration, corresponding to three secondary hydroxyl groups. This supports the pyranosyl ring structure for **2**. The ^{1}H NMR spectrum of **4** (Table 1), showed three doublets at δ 4.87, 4.83, and 4.71, which disappeared by deuteration corresponding to three secondary hydroxyl groups, likewise in accord with the pyranosyl ring structure.

Having the two pyranosyl anomers **2** and **4** on hand, their anomeric assignments from ^{1}H NMR spectral results were not in agreement with their optical rotation properties. The specific rotation at the sodium D-line for compound **2** showed lower specific rotation ($[\alpha]_D + 4.3°$) than compound **4** ($[\alpha]_D + 52.3°$) suggesting the β-D configuration for **2** and the α-D configuration for **4**, according to the Hudson isorotation rules.[11] However, this was not in agreement with their ^{1}H NMR spectral measurements. Compound **2** showed the anomeric proton as a doublet at δ 4.62 having coupling constant $J_{1',2'}$ 9.7 Hz in accord[12–14] with a diaxial orientation of H-1′ and H-2′ of an α-D-$^1C_4$ conformation. On the other hand, compound **4** showed the anomeric proton as a singlet at δ 4.69. This low $J_{1',2'}$ coupling constant value is in accord with the axial equatorial orientation of H-1′ and H-2′ of an β-D-$^4C_1$ conformation (Fig. 1). This was confirmed by the large coupling constant value $J_{3',4'}$ 10.2 Hz for its acetyl derivative **8** (Table 1).

Table 1
^1H NMR chemical shifts[a] (δ) and first-order coupling constants (Hz) for compounds **2**–**12**

Compd	Glycosyl part									2-Phenyl-2H-1,2,3-triazole			
											Phenyl group		
	H-1′	H-2′	H-3′	H-4′	H-5′	H-5″	OH	OAc	Ip	H-5	o-	m-	p-
2[b]	4.62d $J_{1'2'}$ 9.7	3.98dd $J_{2',3'}$ 2.8	3.79m[c]	3.61t $J_{4',5'}$ 3.8	3.79m[c]	3.56d $J_{5',5''}$ 10.8	4.99t 2′-OH, 3′-OH 4.69d J 7.3			8.03s	7.77d J 8.0	7.55dd J 7.7, J 8.1	7.40t
3[b]	4.83d $J_{1'2'}$ 8.1	4.32dd $J_{2',3'}$ 4.1	4.16m	4.16m	3.68dd $J_{4',5'}$ 4.6 $J_{5',5''}$ 11.5	3.54dd $J_{4',5''}$ 5.8	5.2d J 7.3 4.95d J 4.2 4.58t J 5.5			8.12s	7.99t	7.55t	7.41t
4[b]	4.69s	3.85	3.85	3.71m	3.44dd $J_{4',5'}$ 3.3 $J_{5',5''}$ 9.3	3.15t $J_{4',5'}$ 10.7	4.87d J 5.6 4.83d J 5.7 4.71d J 5.0			7.96s	7.95d	7.54t J 8.1	7.39t
5[b]	5.07 $J_{1'2'}$ 5.4	4.18t $J_{2',3'}$ 4.3	4.33dd $J_{3',4'}$ 6.2	3.97m	3.66dd $J_{4',5'}$ 4.1 $J_{5',5''}$ 11.6	3.58dd $J_{4',5''}$ 5.0	5.09d 4.99d 4.89t			8.00s	7.99dd	7.56t	7.40t
6[d]	5.00m[e]	5.88dd J 3.0	5.50m	5.00m[e]	4.03dd $J_{4',5'}$ 2.1	3.92dd $J_{4',5''}$ 2.3 $J_{5',5''}$ 12.9		2.07s 2.15s 2.16s		7.81s	8.04d	7.46t	7.36t
7[f]	5.28d $J_{1',2'}$ 8.1	5.73m	5.73m	4.65m	4.31m	4.31m		2.16s 2.08s 2.07s		7.82s	8.05dd	7.47dd	7.36t
8[f]	4.95s	5.75d $J_{2',3'}$ 2.3	5.22dd $J_{3',4'}$ 10.2	5.35m (sextet)	4.33dd $J_{4',5'}$ 5.6 $J_{5',5''}$ 11.2	3.47t		2.01s 2.02s 2.06s		7.75s	7.96d J 8.4	7.44t J 7.5	7.32t
9[f]	5.52d $J_{1',2'}$ 5.4	5.72m	5.72m	4.50m	4.41s	4.34d $J_{4',5'}$ 2.9 $J_{5',5''}$ 7.8		2.13s 2.12s 1.95s		7.88s	8.00t J 7.9	7.50dd	7.37m
10[f]	5.13d $J_{1',2'}$ 8.3	4.55dd $J_{2',3'}$ 4.2	4.44t $J_{3',4'}$ 3.6	4.18dd	4.06dd	3.94m $J_{4',5'}$ 3.4 $J_{5',5''}$ 13.0			1.485 1.474 (Δδ 0.011)	7.81s	8.04m	7.45t	7.33t
11[b]	4.56d $J_{1',2'}$ 7.4	3.67m–3.82m	3.67m–3.82m	3.67m–3.82m	3.67m–3.82m	3.67m–3.82m	5.07d J 4.6 5.04d J 4.0	(OCH_3) 3.23s		8.03s	8.00d J 7.8	7.56t J 7.8	7.56t J 7.6
11[d]	4.73d $J_{1',2'}$ 3.2	4.07t $J_{2',3'}$ 2.3	4.28d J 1.6	4.12m	3.66m	3.66m	exchanged	(OCH_3) 3.37s		7.89s	8.00d J 8.3	7.47t	7.34t
12[f]	4.75d $J_{1',2'}$ 5.2	4.03dd $J_{2',3'}$ 4.9	5.30dd $J_{3',4'}$ 1.4	5.13m	4.06m			2.09s 1.96s	(OCH_3) 3.41s	7.86s	8.03d J 7.9	7.46t	7.33t

[a] Values for δ for the sugar protons are obtained after the addition of CD_3CO_2D and assigned by ^1H decoupling experiments.

[b] In DMSO-d_6 at 500 MHz.

[c] Overlap between H-3′ and H-5′.

[d] In $CDCl_3$ at 270 MHz.

[e] Overlap between H-1′ and H-4′.

[f] In $CDCl_3$ at 500 MHz.

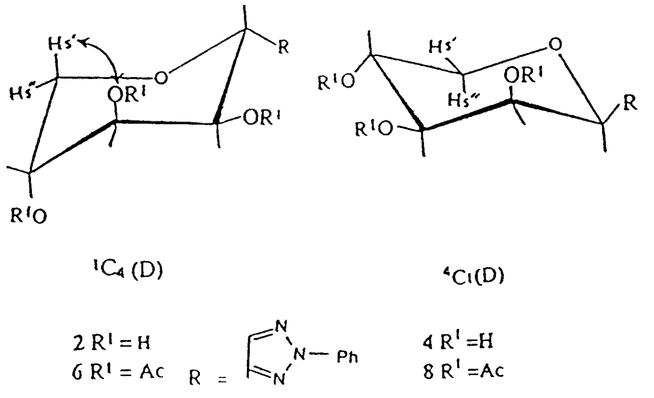


Fig. 1. $^1C_4$(D) and $^4C_1$(D) conformations for compounds **2**, **4**, **6**, and **8**.

Compound **2** was isolated by Peres et al.[15] as a sole *C*-nucleoside reaction product following our route of acid-catalyzed dehydrative cyclization of D-*galacto*-heptulose phenylosazone and subsequent treatment with copper sulfate. It was given the α-D-lyxopyranosyl configuration on the basis of ^{1}H NMR spectral data and periodate oxidation. The contradiction of the rotation results of **2** and **4** with their coupling constant $J_{1',2'}$ values demanded the need of other ^{1}H NMR criteria and other means for anomeric assignment, especially as the two anomers were available.

The chemical shift of the anomeric proton of **4** having a cis arrangement of H-1′ and H-2′ was shown more downfield (δ 4.69) than that for **2** (δ 4.62), in accord[9,12–14] with the β configuration of **4** and α configuration of **2**. However, the acetyl derivative **8** showed, in contrast, the anomeric proton more upfield (δ 4.95) than that of **6** (δ 5.00, overlapped with H-4′) (Table 1). This small chemical shift difference between compounds **4** and **2** and **8** and **6** cannot be used safely for anomeric assignment of this class of compounds on the basis of the chemical shift criteria.

Regarding the ^{13}C NMR chemical shift data (Table 2), the anomeric configuration of *C*-glycopyranosides can be assigned[16–19] by comparison of the ^{13}C NMR chemical shifts for C-1′ and C-5′ when the two anomers are available. The γ-gauche effect[20] predicts that C-1′ and C-5′ of α-glycopyranoside anomers will be shielded with respect to the corresponding carbons of β anomers. Compound **2** showed the anomeric carbon upfield (δ 70.2) than that of

Table 2
^{13}C NMR chemical shifts (δ) for compounds **2**–**5**, **7**, **9**, **11**, and **12**

Compound	Glycosyl part									2-Phenyl-1,2,3-triazole			
						OAc				Phenyl group			
	C-1′	C-2′	C-3′	C-4′	C-5′	CO	CH_3	C-4	C-5	C-*o*	C-*m*	C-*p*	C-a
2 [a]	70.2 [b]	67.6	70.2 [b]	69.6	67.0			139.2	135.2	118.2	129.7	127.5	149.5
3 [a]	75.3	72.0	72.5	80.9	60.3			139.2	134.8	118.3	129.7	127.6	150.2
4 [a]	74.6 [b]	70.3	74.6 [b]	71.2	66.2			139.3	135.6	118.3	129.8	127.6	148.9
5 [a]	80.9	75.1	72.4 [d]	71.8 [d]	60.2			139.3	136.8	118.2	129.8	127.5	148.7
7 [c]	74.2	71.4	75.3	76.6	62.6	170.6 169.6 169.5	20.80 20.51 20.48	139.6	134.2	119.0	129.4	127.8	146.7
9 [c]	74.2	71.8 [d]	72.3 [d]	76.1 [d]	62.9	170.7 169.5 169.2	20.8 20.4 [b] 20.4 [b]	139.6	134.2	118.7	129.3	127.8	145.6
11 [a]	87.0	78.0 [d]	76.7 [d]	76.1 [d]	73.2		(OCH_3) 56.7	139.1	135.2	118.3	129.7	127.7	148.1
12 [c]	85.9	79.0 [d]	76.6 [d]	76.5 [d]	73.0	171.10 170.30	21.6 21.4 (OCH_3) 58.4	140.4	135.5	119.6	130.0	128.3	147.0

[a] In DMSO-d_6 at 125.7 MHz.
[b] Overlapped.
[c] In $CDCl_3$ at 125.7 MHz.
[d] Interchangeable, uncertain.

4 (δ 74.6), in accord with the α configuration of **2** and β configuration of **4**. However, the C-5′ resonance of **2** was not in accord with the γ-gauche effect and was shifted more downfield (δ 67.0) than that of **4** (δ 66.2).

Nuclear Overhauser effect (NOE) measurements are considered a more reliable tool for anomeric assignment,[21,22] and the results of NOE studies were in support of the anomeric configuration of *C*-glycosides.[16,17,23–28] For *C*-glycopyranosides the carbons bonded to the ring oxygen (C-1′, C-5′) place the respective hydrogens at close proximity on the same face of the pyranose ring. For β-D-glycopyranosyl analogs, irradiation of H-1′ gives rise to an NOE effect at H-5′. Irradiation of H-1′ for the acetyl derivative **8** gave rise to 5.7% enhancement of the upfield apparent triplet at δ 3.47 corresponding to the geminal axial proton H-5″ (trans to H-4′). No enhancement was observed at the lowfield equatorial proton H-5′ (cis to H-4′). Similarly, irradiation of H-5″ gave rise to 11% enhancement of the anomeric proton H-1′. This indicates that H-1′ and H-5″ are on the same face of the pyranosyl ring for compound **8** in a β-D configuration with the predominance of the $^4C_1$(D) conformation.

Irradiation of the anomeric proton for compound **2** showed enhancement (5.2%) of the multiplet at δ 3.79 corresponding to the overlapped two protons, H-3′ and the axial geminal proton H-5′ (cis to H-4′). This axial geminal proton H-5′ showed an unexpected downfield shift than the equatorial geminal proton H-5″ (δ 3.56) due to the 1,3-syn interaction between H-5′ and 3′-OH (Fig. 1). No enhancement was observed at the upfield doublet (δ 3.56) corresponding to the shielded equatorial geminal proton H-5″ (trans to H-4′). Similarly, irradiation at the multiplet at δ 3.79 (H-3′, H-5′), gave 10.6% enhancement of the anomeric proton (H-1′). This indicates the presence of H-1′ and H-5′ on the same face of the pyranose ring for **2**, i.e., an α-D configuration with the predominance of the $^1C_4$(D) conformation. These NOE spectral results confirmed the anomeric configuration of **2** as the α-D configuration and **4** as the β-D configuration, despite the lower specific rotation for **2**; ($[\alpha]_D + 4.3°$ than **4**; $[\alpha]_D$ 52.3°). This represents an exception to the Hudson isorotation rules, which should be used with care for anomeric assignment for *C*-nucleosides as the optical rotation may be affected with variation of base moieties.

The β-D-lyxofuranosyl anomer **5** was eluted from the column with 60% aqueous methanol before the α-D-lyxofuranosyl anomer **3** and in lower yield. Periodate oxidation of **3** and **5** consumed one mole of oxidant, in accord with the furanosyl ring structure. The ^{1}H NMR spectrum of **3** and **5** (Table 1) showed two doublets corresponding to two secondary hydroxyl groups and one triplet corresponding to a primary hydroxyl group, all exchangeable by deuteration, which is in support of the furanosyl ring structure.

The anomeric proton H-1′ for **3** was shown as a doublet at δ 4.83 having a coupling constant $J_{1',2'}$ 8.1 Hz. Likewise its acetyl derivative **7** showed the same coupling constant value for the anomeric proton H-1′. Its *O*-isopropylidene derivative **10** did not show the expected decrease in the coupling constant value due to puckering of the furanosyl ring having trans arrangement of H-1′ and H-2′. In addition, the difference ($\Delta\delta$) between the chemical shift of the methyl signals of the 2,2-dimethyldioxolane ring (0.011) is exceptionally low for α anomers (≤ 0.10).[29] This makes the $\Delta\delta$ criterion inapplicable for anomeric assignment. However, nuclear Overhauser effect (NOE) studies on the acetyl derivative **7** showed upon irradiation at H-1′ enhancement (1.1%) of the multiplet corresponding to the geminal protons H-5′, H-5″. Similarly, irradiation of the H-5′, H-5″ multiplet resulted in (1.4%) enhancement of (H-1′). These results indicate the presence of H-1′ and the CH_2OH group on the same face of the furanosyl ring, i.e., the α-D configuration. In addition, the X-ray crystallographic data for **3** (Fig. 2) showed a trans arrangement of H-1′, H-2′ and H-1′, H-4′ that unequivocally assigns the structure and anomeric configuration of **3** as the α-D-lyxofuranosyl configuration. Therefore, the large coupling constant ($J_{1',2'}$ 8.1–8.3 Hz) for compounds **3**, **7** and **10** is an exception to the common coupling constant criterion for anomeric assignment. But, the X-ray result is an unequivocal and overriding proof for the α-D configuration. Further, the bulky anomeric triazole base moiety should prefer-

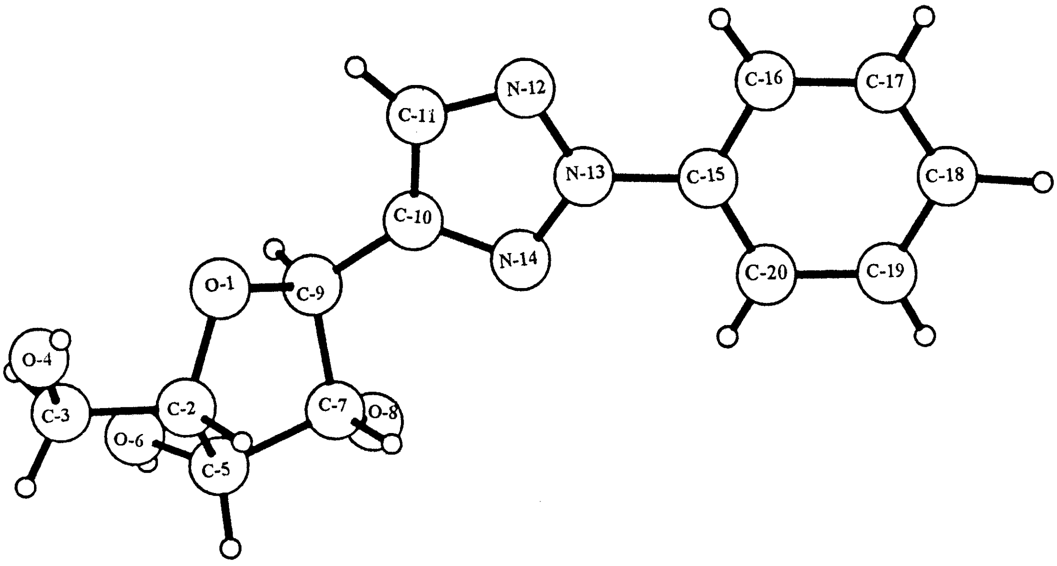


Fig. 2. ORTEP drawing showing the atom numbering for 4-(α-D-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole (**3**).

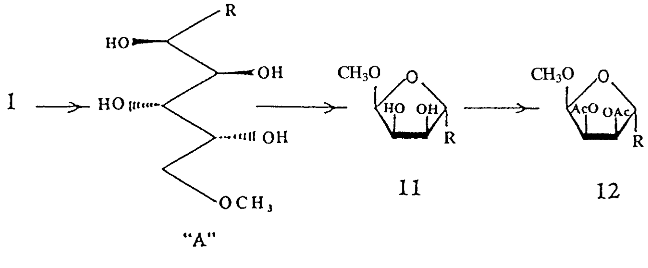
entially occupy a pseudo-equatorial position, and this would explain the larger than usual $J_{1',2'}$ coupling constant value.

The anomeric configuration of the lyxofuranosyl anomer **5**, could not be obtained from the observed coupling constant value $J_{1',2'}$ 5.4 Hz. However, having the two isomers **3** and **5** on hand, the chemical shift of the anomeric proton for **3** having a trans arrangement of H-1′ and H-2′ showed the anomeric proton more upfield (δ 4.83) than that of **5** (δ 5.07), suggesting the cis arrangement of H-1′ and H-2′ for **5**, i.e., the β-D-lyxofuranosyl configuration. The same correlation was observed for the acetyl derivatives **7** and **9** (H-1′ for **9** was shown as a doublet at δ 5.52 and that for **7** at δ 5.28 suggesting a cis arrangement of H-1′ and H-2′ for **9** and trans arrangement for **7**). The β configuration of **5** was confirmed from the nuclear Overhauser effect of its acetyl derivative **9**. Irradiation of H-1′ showed enhancement (2.6%) at H-4′ (H-2′, H-3′ were overlapped and showed 8.8% enhancement). Similarly, irradiation at H-4′ showed enhancement (3.4%) at H-1′. This indicated the presence of H-1′ and H-4′ at the same face of the furanosyl ring, i.e., the β-D configuration for **9**.

The specific rotation for the α anomer **3** was lower than that for **5** ($[\alpha]_D$ in methanol; **3**, $[\alpha]_D + 39.3°$; **5**, $[\alpha]_D + 72.7°$), which is opposite to that predicted by the Hudson isorotation rules.[11] This represents an additional exception for the Hudson rotation rules at the furanosyl anomers.

The D-lyxopyranosyl anomers **2** and **4** were isolated from the acid-catalyzed dehydrative cyclization of **1** as the thermodynamic products. Analogous pyranosyl anomers were isolated from the dehydrative cyclization of their D-*galacto*-pentahydroxypentyl heterocyclic precursors.[30–33] However, analogous kinetic D-lyxofuranosyl products similar to compounds **3** and **5**, have not been isolated before as far as we know from the dehydration of pentahydroxypentyl heterocyclic analogs having the D-*galacto* configuration. Compounds **2** and **3** were obtained from **1** with inversion at C-1′, whereas **4** and **5** were obtained without inversion. The low yield of **5** has been explained by its formation through a transition state[30] that is destabilized by steric repulsions[34] between adjacent cis groups.

Periodate oxidation of the byproduct **11** (Scheme 2) consumed one mole of oxidant in



Scheme 2.

Table 3
Summary of crystal data parameters and results for compound **3**

Temperature (K)	294
Space group	$P2_1$
a (Å)	4.749(2)
b (Å)	10.572(2)
c (Å)	13.141(5)
V (Å^3)	645.4(4)
Molecular weight	277.3
Z	2
D_{calcd} (g/mL)	1.430
Crystal dimensions (mm)	$0.034 \times 0.280 \times 0.221$
Absorption coefficient (1/cm 1.01)	
Scan range (°)	Mo $K_{\alpha 1}$ −0.8 to Mo $K_{\alpha 2}$ +0.9
Background time ratio	0.8
2θ (°)	50
Data collected	1452
Data $>3\sigma(I)$	1652
Final R	0.051
Final R_w	0.040
Residual (e/Å^3)	0.24
Goodness-of-fit	0.50

accord with the furanose ring structure. Its ^{1}H NMR spectrum in Me$_2$SO-d_6, showed two doublets at δ 5.07 and 5.04 that were exchangeable after deuteration, corresponding to two secondary hydroxyl groups. The methoxyl group signal was shown at δ 3.23, in accord with 5′-*O*-methyl furanosyl ring structure. The observed signal for the anomeric proton was solvent dependent. In Me$_2$SO-d_6, it was shown as a doublet at δ 4.56 having coupling constant $J_{1',2'}$ 7.4 Hz. However, in CDCl$_3$ it was shown as a doublet at δ 4.73 having coupling constant $J_{1',2'}$ 3.2 Hz. The latter may suggest a trans arrangement of H-1′ and H-2′, i.e., the α-D configuration. This difference in the coupling constant values in Me$_2$SO-d_6 and CDCl$_3$ may be explained by a change in the conformation of the 5′-*O*-methyl furanosyl ring in the two different solvents. Its acetyl derivative **12** showed the anomeric proton as a doublet at δ 4.75 having a coupling constant $J_{1',2'}$ 5.2 Hz that cannot support the anomeric configuration. Compound **11** may be obtained by 5′-methylation of the major lyxofuranosyl anomer **3**, having the α-D configuration. The formation of **11** can be also explained by methylation of the primary hydroxyl group of **1** in the strongly acidic methanolic sulfuric acid solution, giving the intermediate 6-*O*-methyl derivative ‘A’ (Scheme 2). Subsequent cyclization of ‘A’ through the sterically favored direction gives the α anomer **11**.

X-ray structure determination of compound **3**.—The structure and anomeric configuration of **3** was supported by crystallographic data. The numbering scheme and overall conformation of crystals of **3** are shown in Fig. 2.

Single crystals of **3** were grown from a water–methanol solution and mounted on a Syntex P2$_1$ diffractometer. Lattice parameters were determined from a least-squares refinement of 15 reflection settings obtained from an automatic centering routine.

Intensity data were obtained using Mo K$_\alpha$ radiation monochromatized from a graphite crystal whose diffraction vector was parallel to the diffraction vector of the sample. In the subsequent refinement the function $\Sigma\, w(|F_o| - |F_c|)^{35}$ was minimized where $|i_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The agreement indicates $i = \Sigma||F_o| - |i_c||/\Sigma|F_o|$ and $R_w = [\Sigma\, i(|F_o| - |F_c|)^2/\Sigma_i|F_o|^2]^{1/2}$ were used to evaluate the results. The atomic scattering factors are from the International Tables for X-ray Crystallography.[35]

Computations were carried out on an Amdahl 5860 computer. The structure was solved using the direct-methods program MLTTAN78 by Peter Main. Computer programs used during the structural analysis were from the SHELX program package by George Sheldrick, Institute für Anorganische Chemie der Universität Gottingen, Germany. Other programs used included ORTEP, a thermal ellipsoidal drawing program by C.K. Johnson.

Table 3 lists the crystal data. It contains a summary of data collection, conditions, and the least-squares refinement results using anisotropic thermal parameters for all non-hydrogen atoms. Hydrogens were located by difference Fourier methods and refined with fixed U_{eq} values (isotropic temperature factors) of 0.05. The data were corrected for absorption. Table 4 shows the fractional atomic coordinates and final positional parameters with estimated standard deviations. Anisotropic thermal parameters with their estimated standard deviations, bond distances, and angles are available as supplementary material, as well as listings of observed and calculated structure factor amplitudes.

3. Conclusions

The anomeric configuration of the pyranosyl *C*-nucleoside anomers **2** and **4** were determined from their $J_{1',2'}$ coupling constant values. Compound **2** was assigned the α-D-lyxopyranosyl configuration and $^{1}C_{4}$(D) conformation. Compound **4** was given the β-D-lyxopyranosyl configuration and $^{4}C_{1}$(D) conformation. The anomeric ^{1}H and ^{13}C chemical shift values supported this assignment. This was confirmed by the NOE measurements for compound **2** and the acetyl derivative **8**. The pyranosyl anomers **2** and **4** are formed from the acid-catalyzed dehydration of **1** as thermodynamic products with the preponderance of the α-pyranosyl anomer **2**.

The anomeric configuration of the furanosyl anomers **3** and **5** could not be assigned from their $J_{1',2'}$ coupling constant values. The NOE of the acetyl derivative **7** was in accord with the α-D-lyxofuranosyl configuration, which was unequivocally confirmed by the X-ray crystallography of **3**. The β-D-lyxofuranosyl configuration for **5** was assigned by comparing the chemical shift values of the anomeric protons for **3** and **5** and was confirmed by NOE of the acetyl derivative **9**. The furanosyl anomeric pair **3** and **5** were obtained from the dehydration of **1** as kinetic products with the preponderance of the α-furanosyl anomer **3**. Compounds **2** and **3** were obtained from **1** with inversion of the configuration at C-1′, whereas **4** and **5** were obtained without inversion.

Table 4
Fractional atomic coordinates

Atom	*x*	*y*	*z*	U_{eq}
O-1	0.2157(8)	0.191(18)	0.0270(3)	0.038
C-2	0.2940(13)	0.266(18)	−0.0546(4)	0.032
C-3	0.0997(15)	0.237(18)	−0.1566(5)	0.038
O-4	0.1331(16)	0.108(18)	−0.1876(5)	0.044
C-5	0.2816(13)	0.402(18)	−0.0166(4)	0.031
O-6	−0.0128(11)	0.438(18)	−0.0322(4)	0.039
C-7	0.4142(12)	0.385(18)	0.0991(4)	0.030
O-8	0.3607(8)	0.485(18)	0.1622(3)	0.038
C-9	0.2830(12)	0.261(18)	0.1243(4)	0.030
C-10	0.4674(11)	0.182(18)	0.2064(4)	0.029
C-11	0.4310(16)	0.057(18)	0.2349(5)	0.041
N-12	0.6384(12)	0.026(18)	0.3148(4)	0.043
N-13	0.7927(9)	0.131(18)	0.3330(3)	0.033
N-14	0.6990(10)	0.228(18)	0.2697(3)	0.033
C-15	1.0320(12)	0.140(18)	0.4194(4)	0.035
C-16	1.1999(14)	0.246(18)	0.4321(5)	0.041
C-17	1.4272(14)	0.253(18)	0.5177(5)	0.051
C-18	1.4858(15)	0.156(18)	0.5891(5)	0.051
C-19	1.3127(17)	0.051(18)	0.5732(5)	0.055
C-20	1.0827(15)	0.041(18)	0.4897(5)	0.046

The assignment of the anomeric configuration for the pyranosyl and furanosyl anomers from their NMR spectral data was not in agreement with their optical rotation data, which represents a violation of the Hudson isorotation rules. The later should be used with care for *C*-nucleosides and should be supported by more than one method for anomeric assignment.

4. Experimental

General.—Melting points were determined with a Fisher–Johns instrument. Evaporations were performed under diminished pressure below 60 °C. Thin-layer chromatography (TLC) was conducted on Silica Gel (Kieselgel G, Merck) with solvent A (3:1 benzene–EtOH), B (10:1 $CHCl_3$–MeOH), C (2.5:3 EtOAc–hexane), D (3:1 EtOAc–hexane), or E (5:1 toluene–EtOH). Compounds were detected under short UV light at 254 nm. IR spectra were recorded with a Perkin–Elmer Lambda 48 instrument. Optical rotations and ORD measurements were obtained at 20 ± 2 °C with a Perkin–Elmer 241 Polarimeter 10 cm, 1 mL microcell. ^{1}H NMR spectra were recorded with a General Electric 500 MHz, Nicolet 470 MHz, Bruker WP 270 SY MHz, and Bruker AM 500 MHz spectrometers using tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded with the General Electric 500 instrument at 125.0 MHz or the Bruker 500 instrument at 125.7 MHz. Assignment of peaks was verified by ^{1}H–^{13}C COSY experiments. Chemical shifts in δ ppm were referenced to $CDCl_3$ (77.7), Me_2SO-d_6 (39.50), or tetramethylsilane Me_4Si (TMS) as internal standards. NOE experiments were obtained using the standard Bruker NOEDIFF microprogram. The anomeric protons were preirradiated for 15 scans at 35 dB attenuation of the low power decoupler (≈ 0.4 W). This was altered every eight scans with off-resonance irradiation for the spectra that were to be subtracted. Mass spectra were recorded with a Finnigan 4021 low-resolution EI–CI spectrometer at 70 eV. High-resolution mass spectra were recorded with a VG analytical model 70-250 spectrometer. Combustion analyses were performed in the Department of Chemistry, Cairo University, Cairo, Egypt and M-H-W Laboratories, Phoenix, AZ, USA.

*4-(α-D-Lyxopyranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**2**).—A suspension of 4-(D-*galacto*-pentitol)-1-yl-2*H*-1,2,3-triazole (**1**)[36] (3 g), in 20% methanolic sulfuric acid (50 mL) (made by adding one volume of concd H_2SO_4 to four volumes of MeOH) was refluxed on a water bath for 10 h. Complete dissolution was obtained after 5 h, TLC indicated disappearance of the starting material after 8 h. The soln was diluted with water (20 mL), MeOH was evaporated under reduced pressure, and the soln was continuously extracted with $CHCl_3$. The $CHCl_3$ layer was separated, washed with water, $NaHCO_3$, and water, then dried over anhyd sodium sulfate. The $CHCl_3$ soln was concd into a small volume, giving colorless needles of **2** (yield 800 mg). The mother liquor was evaporated to a syrup which was chromatographed on a column (2 × 46 cm) of Dowex-1 X 8 (OH^-) ion-exchange resin (200–400 mesh) and eluted with 30, 60, and 90% aq MeOH. Fractions (15 mL) at a rate of 1.5 mL/min were collected. The 60% aq MeOH afforded a further crop of **2**; 150 mg, total yield of **2**, 950 mg (34%). It was recrystallized from MeOH–benzene as colorless needles mp 129–130 °C (Lit[10] mp 130–131 °C). R_f 0.34 (A); $[\alpha]_D^{22} + 4.3°$ (*c* 2.4, MeOH); ORD (MeOH): $[\phi]_{589} + 11.9°$, $[\phi]_{578} + 12.4°$; $[\phi]_{546} + 14.7°$; $[\phi]_{436} + 30.5°$; $[\phi]_{365} + 63.6°$ (for ^{1}H and ^{13}C NMR see Tables 1 and 2); periodate consumption 2.00 mol equiv (based on mol wt 277). In a control experiment using methyl α-D-mannopyranoside under the same conditions for all compounds, 2.04 mol equiv of periodate was consumed (based on mol wt 194).

*4-(2,3,4-Tri-*O*-acetyl-α-D-lyxopyranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**6**).—Compound **6** was prepared as described previously[10] and was identical with the authentic product by ^{1}H NMR spectroscopy. For ^{1}H NMR spectral data see Table 1.

*4-(β-D-Lyxopyranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**4**).—Compound **4** was isolated from the Dowex resin column chromatography of the syrup obtained after the partial separation of **2** and eluted with 60% aq MeOH after elution of **2**. Identical fractions were collected and evaporated to dryness giving a precipitate; yield 80 mg. The product was recrystallized as colorless needles mp 203–204 °C (Lit[10] mp 204 °C); $[\alpha]_D^{22} + 52.3°$ (*c* 0.52, MeOH); ORD (MeOH): $[\phi]_{589} + 144.9°$, $[\phi]_{578} + 152.9°$; $[\phi]_{546} + 179.2°$; $[\phi]_{436} + 357.9°$; $[\phi]_{365} + 728.5°$; R_f 0.31 (A) (for ^{1}H and ^{13}C NMR data see Tables 1 and 2); periodate consumption 1.98 mol equiv.

*4-(Tri-*O*-acetyl-β-D-lyxopyranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**8**).—Compound **8** was prepared as described previously.[10] It showed identical ^{1}H NMR spectral measurements. For ^{1}H NMR spectral data see Table 1.

*4-(α-D-Lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**3**).—Compound **3** was separated from the resin column by elution with 60% aq MeOH after elution of **4**; yield 280 mg, mp 138–140 °C; R_f 0.32 (E); $[\alpha]_D + 39.3°$ (*c* 1.08, MeOH); ORD (MeOH): $[\phi]_{589} + 108.8°$, $[\phi]_{578} + 113.0°$; $[\phi]_{546} + 127.4°$; $[\phi]_{436} + 206.4°$; $[\phi]_{365} + 308.3°$ (for ^{1}H and ^{13}C NMR data see Tables 1 and 2); EIMS: *m*/*z* 278 (10, M + 1), 277 (4, M), 260 (6, M − OH), 259 (38, M − H_2O), 200 (23, M − Ph), 188 (38, M − 89), 187 (17, MH − PhN), 186 (7, M − PhN), 175 (18, BCH_2OH), 174 (100, BCHOH), 173 (8, BCHO), 158 (20, BCH_2), 92 (13, PhNH), 91 (36, PhN), and 77 (27, Ph); periodate consumption 1.09 mol equiv (based on mol wt 277). Anal. Calcd for $C_{13}H_{15}N_3O_4$: C, 55.86; H, 5.66; N, 15.19. Found: C, 56.30; H, 5.45; N, 15.15.

*4-(2,3,4-Tri-*O*-acetyl-α-D-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**7**).—Compound **3** (38 mg) was dissolved in pyridine (1 mL) and treated with Ac_2O (1 mL), and the mixture was kept for 24 h at rt. The mixture was evaporated to dryness, and traces of pyridine were removed by spin coevaporation with toluene and $CHCl_3$. The resulting syrup was purified by chromatography on a short column (1×10 cm) of silica gel and eluted with solvent (C): colorless syrup; yield 40 mg; R_f 0.81 (E) (for ^1H and ^{13}C NMR data see Tables 1 and 2); EIMS: *m*/*z* 404 (0.2, M + 1), 403 (0.1, M), 344 (4, M − OAc), 343 (17, M − AcOH), 283 (3, M − 2 AcOH), 242 (6, M − 2 OAc–Ac), 241 (29, M − OAc–AcOH–Ac), 224 (66, M − 2 AcOH–OAc), 188 (5, $BHCH_2CHO$), 187 (7, BCH_2-CHO), 174 (13, BCHOH), 173 (4, BCHO), 172 (9, BCO), 86 (19, M − BCHOAc–OAc–CH_2CO), 84 (31, M − BCH_2OAc–AcOH–CH_3CO), 77 (8, Ph), and 43 (100, CH_3CO); HRCIMS (isobutane): Found 404.1453; Calcd for $C_{19}H_{22}N_3O_7$ 404.1458.

*4-(2,3-*O*-Isopropylidene-α-*D*-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**10**).—Compound **3** (50 mg) was stirred in a soln of 2,2-dimethoxypropane (5 mL) and a catalytic amount of *p*-toluenesulfonic acid (4 mg) for 1 h at rt. TLC indicated the reaction to be complete. The mixture was poured into satd aq $NaHCO_3$ solution and extracted with $CHCl_3$. The $CHCl_3$ soln was dried over anhyd magnesium sulfate. The organic extract was filtered, evaporated to dryness, and the residue was recrystallized from petroleum ether (40–60 °C) to give colorless needles; yield 23 mg; mp 120–121 °C; R_f 0.37 (C) (for ^1H and ^{13}C NMR data see Tables 1 and 2); EIMS: *m*/*z* 317 (5, M), 302 (5, M − CH_3), 259 (4, M − CH_3COCH_3), 200 (10, M − CH_3COCH_3 − CH_2OH–H_2O), 187 (26, BCH_2CHO), 174 (15, BCHOH), 173 (5, BCHO), 172 (4, BCO), 91 (23, PhN), 77 (24, Ph), and 43 (100, CH_3CO); HREIMS: Found [M^+] 317.1376; Anal. Calcd for $C_{16}H_{19}N_3O_4$ 317.1376. Calcd for $C_{16}H_{19}N_3O_4$: C, 60.56; H, 6.04; N, 13.24. Found: C, 60.42; H, 6.09; N, 13.20.

*4-(β-*D*-Lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**5**).—Compound **5** was eluted by 60% aq MeOH from the resin column after the separation of compounds **2**, **4** and **3**, respectively. It was recrystallized from $CHCl_3$–petroleum ether (bp 60–80 °C) as colorless needles; yield 10 mg; mp 86–87°; R_f 0.31 (E), $[\alpha]_D^{22}$ + 72.7° (*c* 1.08, MeOH); ORD (MeOH): $[\phi]_{589}$ + 201.0°, $[\phi]_{578}$ + 211.0°; $[\phi]_{546}$ + 244.6°; $[\phi]_{436}$ + 472.0°; $[\phi]_{365}$ + 950.0°; $\nu_{\max}^{\text{KBr}}$ 3340 (OH), 1605 (C=N), and 1500, 750 (Ph) cm^{-1} (for ^1H and ^{13}C NMR data see Tables 1 and 2); EIMS: *m*/*z*: 278 (2, M + 1), 277 (3, M), 200 (24, M − Ph), 188 (24, M − 89), 187 (7, MH − PhN), 175 (13, BCH_2OH), 174 (100, BCHOH), 173 (5, BCHO), 158 (10, BCH_2), 92 (9, PhNH), 91 (34, PhN), and 77 (23, Ph); periodate consumption 1.066 mol equiv. Anal. Calcd for $C_{13}H_{15}N_3O_4$: C, 56.30; H, 5.45; N, 15.15. Found: C, 56.38; H, 5.63; N, 15.46.

*4-(2,3,5-Tri-*O*-acetyl-β-*D*-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**9**).—Compound **5** (10 mg) was acetylated with a mixture 1:1 of pyridine–Ac_2O (2 mL) for 12 h at rt and processed as described for **7** to give colorless syrup R_f 0.73 (E) (for ^1H and ^{13}C NMR data see Tables 1 and 2); EIMS: *m*/*z* 404 (2, M + 1), 403 (9, M), 343 (8, M − AcOH), 283 (3, M − 2 AcOH), 242 (7, M − 2 OAc–Ac), 241 (25, M − AcOH–OAc–Ac), 224 (44, M − 2 AcOH–OAc), 200 (8), 187 (7, BCH_2CHO), 174 (20, BCHOH), 173 (5, BCHO), 91 (9, PhN), 77 (8, Ph), and 43 (100, CH_3CO); HREIMS: Found 403.1392; Calcd for $C_{19}H_{21}N_3O_7$ 403.1379.

*4-(5-*O*-Methyl-α-*D*-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**11**).—Compound **11** was eluted from the resin column with 90% MeOH and recrystallized from dilute MeOH; yield 149 mg; mp 174–176 °C; R_f 0.42 (A); $[\alpha]_D^{22}$ + 74.3° (*c* 0.53, MeOH), $\nu_{\max}^{\text{KBr}}$ 3340 (OH), 1595 (C=N), and 1495, 740 (Ph) cm^{-1} (for ^1H and ^{13}C NMR data see Tables 1 and 2); EIMS: *m*/*z* 291 (1, M), 189 (19, $BHCH_2CHOH$), 188 (100, BCH_2CHOH), 91 (12, PhN), and 77 (10, Ph); periodate consumption 1.01 mol equiv. Anal. Calcd for $C_{14}H_{17}N_3O_4$: C, 57.72; H, 5.88; N, 14.43. Found: C, 57.62; H, 5.91; N, 14.33 (mol wt 291).

*4-(2,3-Di-*O*-acetyl-5-*O*-methyl-α-*D*-lyxofuranosyl)-2-phenyl-2*H*-1,2,3-triazole* (**12**).—Compound **11** (10 mg) was acetylated with a mixture 1:1 pyridine–Ac_2O (2 mL) for 24 h at rt. The mixture was processed as described for **9** to give a colorless syrup; R_f 0.46 (C) (for ^1H and ^{13}C NMR data see Tables 1 and 2); CIMS (isobutane): 377 (4, MH_2), 376 (17, MH), 345

(6, MH $-$ OCH_3), 344 (32, M $-$ OCH_3), 285 (18, M $-$ OCH_3 $-$ OAc), 284 (100, M $-$ OCH_3 $-$ AcOH), 226 (17, M $-$ OCH_3 $-$ 2 OAc), 188 (22, BCH_2CHOH), 187 (22, BCH-CHOH), 174 (4, BCHOH), and 77 (2, Ph); EIMS: *m/z* 375 (1, M), 284 (1), 189 (13), 188 (100, BCH_2CHOH), 187 (30), 77 (5, Ph), and 43 (48, CH_3CO); HREIMS: Found: 376.1517; Calcd for $C_{18}H_{22}N_3O_6$: 376.1509.

5. Supplementary material

Full crystallographic details, excluding structure features, have been deposited with the Cambridge Crystallographic Data Centre, position number CCDC 149569. These data may be obtained upon request from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Tel.: + 44-1223-336408; fax: + 44-1223-336033; e-mail deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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