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Preparation and reactions of sugar azides with alkynes: synthesis of sugar triazoles as antitubercular agents☆

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Abstract—5-Azido-5-deoxy-*xylo*-, *ribo*-, and arabinofuranoses were prepared by the reaction of the respective 5-*O*-(methanesulfonyl) or *p*-toluenesulfonyl derivatives with NaN_3 in DMF. The intermediate 5-azido-5-deoxy glycofuranoses on 1,3-cycloaddition with different alkynes in the presence of $CuSO_4$ and sodium ascorbate gave the corresponding sugar triazoles in very good yields. The synthesized sugar triazoles were evaluated for their antitubercular activity against *Mycobacterium tuberculosis H37Rv*, where one of the compounds displayed mild antitubercular activity in vitro with MIC 12.5 μg/mL.

Keywords: 1,3-Cycloaddition; Glycosyl azide; Sugar triazole; Sodium ascorbate

1. Introduction

Synthesis of glycoconjugates and their utilization with an objective to exert a fine control over a plethora of biological functions has been a key research area in recent times.[1,2] Glycoconjugates are implicated in one or the other way in combating a number of metabolic disorders, as well as parasitic and infectious diseases.[2–5] The azido sugars are known as versatile starting materials in accessing a number of biologically active compounds, including amino sugars, nucleosides and many other glycosylated heterocycles.[2,6,7] The term 'click chemistry' coined by Sharpless and co-workers[8] has opened a new chapter in the area of glycoconjugates and macromolecules bearing the triazolyl moiety by cycloaddition of acetylenic compounds with azides. Copper-catalyzed triazole synthesis was first reported by Tornoe et al.,[9] and this work is getting great applicability nowadays for selective triazole synthesis. Carbohydrate-based triazoles are endowed with numerous biological activities including the very recently reported inhibitions of galectins-1 and galectins-3.[10] The galectins are important during cellular development and differentiation stages and under physiological or pathological conditions. They are also involved in the infectivity of the human immunodeficiency virus (HIV).[11] Our interest in triazolyl glycoconjugates emerged during our quest to discover new antitubercular agents from sugars[12] as certain triazoles possess potent antitubercular activity.[13–15] The implication of sugar triazoles in HIV infectivity[11] as mentioned above would be beneficial in the search for new drugs for treating tuberculosis in AIDS patients. Keeping in mind the above facts, we have synthesized sugar triazoles starting with three pentofuranoses, D-xylose, D-ribose and D-arabinose, and have evaluated them for their antitubercular potential in vitro.

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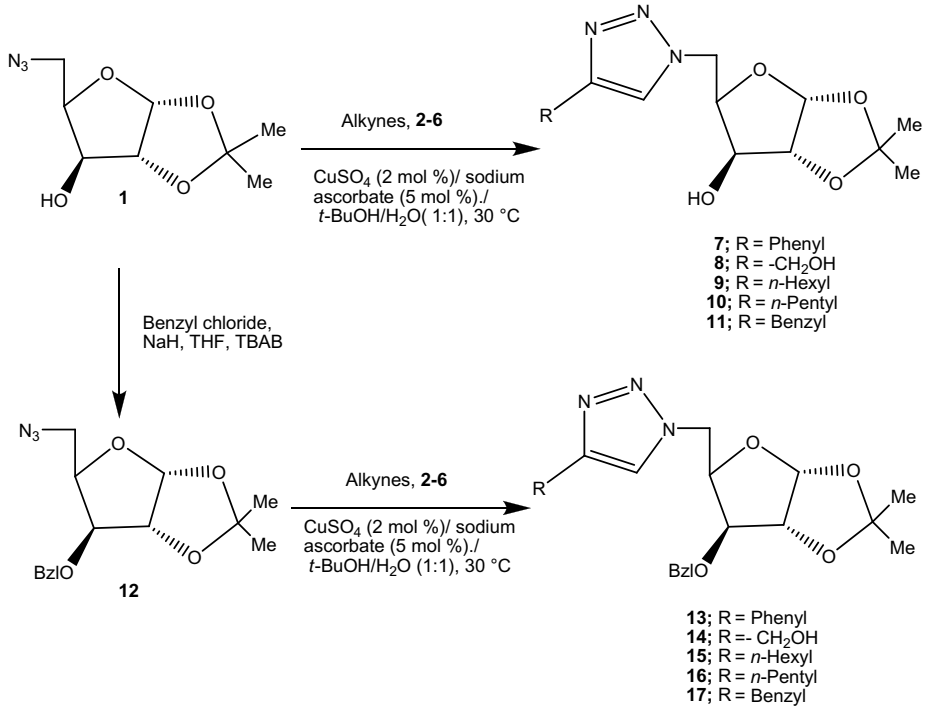
2. Results and discussion

5-Azido-5-deoxy-D-*xylo*-, D-*ribo*- and D- *arabino*-furanoses were prepared from D-xylose, D-ribose and D-arabinose, respectively, using the literature methods of protection and modification. Thus, the reaction of 5-*O*-(*p*-toluenesulfonyl)-α-D-xylofuranose[16] with sodium azide in anhydrous DMF at 90–100 °C led to the formation of 5-azido-5-deoxyxylofuranose (**1**)[17] in >95% yield. The structure of compound **1** was in accordance to its spectroscopic data and microanalysis. In the IR spectrum, absorption spectrum at 2104 cm^{-1} evidenced the presence of an azido group; while in its ^1H NMR and ^{13}C NMR spectra the signals were observed at their usual chemical shifts.[17]

1,3-Dipolar cycloaddition of the above xylofuranosyl azide **1** with different alkynes, viz. phenylacetylene (**2**), propargyl alcohol (**3**), 1-octyne (**4**), 1-heptyne (**5**), and 3-phenyl-1-propyne (**6**) was carried out at ambient temperature in the presence of $CuSO_4$ and sodium ascorbate in a mixture of 1:1 *t*-BuOH–H_2O as reported by Sharpless and co-workers (Scheme 1).[8a] Cycloaddition of phenylacetylene (**2**) with 5-azido-5-deoxy-1,2-*O*-isopropylidne-α-D-xylofuranose (**1**) in the presence of $CuSO_4$ (2 mol %) and sodium ascorbate (5 mol %) resulted in 1-(5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-phenyl-1*H*-1, 2,3-triazole (**7**) in 88% yield. We did not observe the formation of any other product in the reaction (TLC). The structure of triazolyl xylofuranose **7** was established on the basis of its spectroscopic data and HRMS. ESIMS of compound **7** displayed $[M+H]^+$ at 318 amu corresponding to $[M+H]^+$. The ^1H and ^{13}C NMR spectrum of the compound was similar to that reported earlier.[18,20] The anomeric proton of the furanose ring appeared at δ 6.01 (d, $J = 3.6$ Hz), while H-2 appeared at δ 4.84 (d, 1H, $J = 5.1$ Hz), H-3 at δ 4.33 (dd, 1H, $J = 4.9$ Hz, H-3), H-4 and H-5 appeared as a multiplet at δ 4.51–4.65. The only proton of the triazolyl ring was apparent as a singlet at δ 7.94. In the ^{13}C NMR spectrum, C-1 of the furanose sugar appeared at δ 105.3, while C-2, C-3, C-4 and C-5 appeared at δ 74.9, 79.7, 85.8 and 49.5, respectively. The triazolyl C-4 and C-5 were observed at δ 148.2 and 121.7, respectively, a characteristic feature of the ^{13}C NMR spectra of 1,4-regioisomers.[19]

Similarly, the reaction of the above 5-azido-5-deoxy-xylofuranose derivative **1** with other alkynes **3**, **4**, **5** and **6** separately led to the formation of respective 1-xylofuranosyl triazoles **8**–**11**, in 82–97% yields, respectively. The structures of all the compounds were in agreement with their spectroscopic data and microanalyses. All the compounds displayed $[M+H]^+$ corresponding to their molecular formulae. In the ^1H NMR spectra, the sugar ring protons, H-5 of the sugar moiety and the only proton of the triazolyl ring were observed as usual. It is important to mention that compounds **7** and **8** were prepared earlier by other workers[18,20] on refluxing the 5-azido-5-deoxy xylofuranose **1** with phenylacetylene and propargyl alcohol in toluene, respectively, in good yields. With propargyl alcohol they have reported a



Scheme 1. Synthesis of 4-alkyl/aryl-1-(5-deoxy-1,2-*O*-isopropylidene-D-xylofuranosyl)-1*H*-1,2,3-triazoles (**7**–**11** and **13**–**17**).

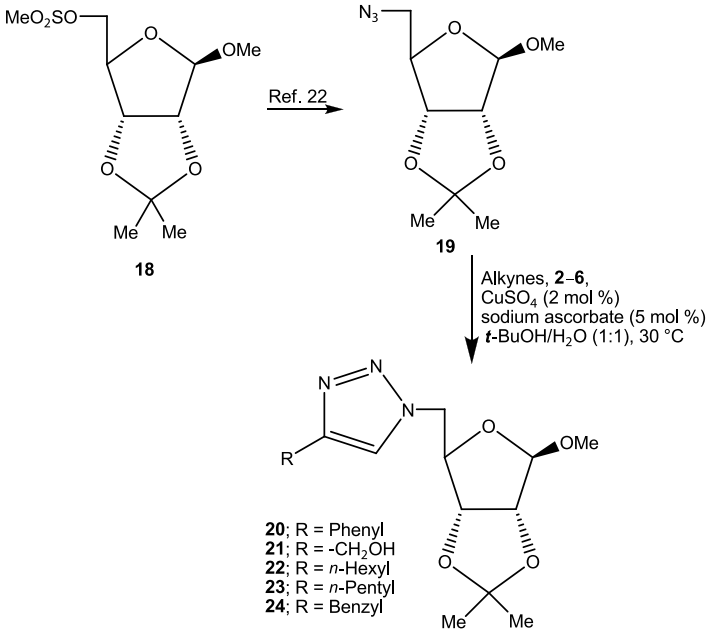
mixture of inseparable regioisomeric triazoles, but in our method all the reactions are regioselective, and also the time requirement is considerably reduced.

To determine the steric effect of the 3-*O*-substituent in the xylofuranose ring on the cycloaddition reaction, 5-azido-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidne-α-D-xylofuranose (**12**) was prepared by benzylation of the above compound **1** with benzyl chloride. Cycloaddition of 5-azido-3-*O*-benzylxylofuranose derivative **12** with the above alkynes **2**–**6** separately as above in the presence of $CuSO_4$ and sodium ascorbate in a mixture of *t*-BuOH–H_2O afforded the respective triazolyl 3-*O*-benzylxylofuranoses **13**–**17** in good yields (Table 1). As evident from Table 1, the yield and reaction times of substrate **12** with alkynes **2**–**6** to give products **13**–**17** are almost the same as with xylofuranosyl azide **1**; thus, the substituent at C-3 in the sugar ring does not affect the course of the reaction. The structures of all the compounds **13**–**17** were in accord with their spectroscopic data and microanalysis.

The ribofuranosyl triazoles as shown in Scheme 2 were prepared from methyl 2,3-*O*-isopropylidene-β-D-ribofuranoside.[21] The latter on reaction with methanesulfonyl chloride led to the formation of 5-*O*-methanesulfonyl ribofuranose derivative (**18**),[22] which on subsequent treatment with NaN_3 in DMF as above led to the formation of methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranoside (**19**)[22,23] in 90% yield. The IR spectrum of this compound displayed the characteristic azido stretching frequency at 2104 cm^{-1}. In the ^1H NMR spectrum, the six protons of the two *gem*-dimethyl groups of the sugar moiety appeared as two singlets at δ 1.31 and 1.48, while H-1 of the furanose ring appeared as a singlet at δ 4.95, H-2 and H-3 both as singlets at δ 4.57, and H-4 as a triplet at δ 4.26 ($J = 7.2$ Hz). On the other hand, two protons of H-5

Table 1. Preparation of sugar triazoles (**7**–**11**) and (**13**–**17**) by the reaction of 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**1**) and 5-azido-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**12**) with different alkynes **2**–**6**

Entry no.	Alkyne	Product	Reaction time (h)	Yield (isolated) (%)
1	Phenylacetylene	**7**	6	88
2	Propargyl alcohol	**8**	3	97
3	1-Octyne	**9**	8	82
4	1-Heptyne	**10**	8	84
5	3-Phenyl-1-propyne	**11**	7	84
6	Phenyl acetylene	**13**	7	72
7	Propargyl alcohol	**14**	3.5	94
8	1-Octyne	**15**	8	82
9	1-Heptyne	**16**	7	90
10	3-Phenyl-1-propyne	**17**	8	91



Scheme 2. Synthesis of 4-alkyl/aryl-1-(5-deoxy-2,3-*O*-isopropylidene-β-D-methyl ribofuranosid-5-yl)-1*H*-1,2,3-triazoles (**20**–**24**).

were observed at two different field strengths as multiplets at δ 3.21 and 3.39. In the ^{13}C NMR spectrum C-1, C-2, C-3, C-4 and C-5 appeared at δ 110.2, 82.4, 85.5, 85.7 and 54.1, respectively. Cycloaddition of azido ribofuranose **19** with the above alkynes **2–6** in the presence of $CuSO_4$ and sodium ascorbate as above separately yielded the respective ribofuranosyl triazoles **20–24** in good yields (Table 2). The only proton of the triazolyl ring (H-5) in all the sugar triazoles was observed as a singlet in the range of δ 7.3–7.8. The characteristic C-4 and C-5 of the 1,4-regioisomers in triazolyl ring appeared at around δ 148 and 120, respectively, in the ^{13}C NMR spectra of all the samples (Scheme 3).

Finally, methyl 5-azido-5-deoxy-α-D-arabinofuranoside (**25**)[24] was prepared starting from methyl D-arabinofuranoside.[25] Reaction with *p*-toluenesulfonyl chloride at low temperature gave predominantly the methyl 5-*O*-(*p*-toluenesulfonyl)-D-arabinofurnoside.[26] The latter on treatment with sodium azide in DMF gave the required intermediate methyl 5-azido-5-deoxy-D-arabinofuranoside (**25**) in good yield. The reaction of arabinofuranoside **25** with different alkynes **2–6** separately resulted in the required respective methyl α-D-arbinofuranosyl-1,2,3-triazoles **26–30** in good yields (Table 3). As compared to the xylose and ribose series of triazoles, the yield of arabinofuranose triazoles is reduced even after prolonged reaction. It may be due to the presence of a hydroxyl group in the sugar ring of compound **25**. However, the presence of a hydroxyl group in the alkyne (propargyl alcohol) again results in increased yield and reduced reaction time. The 1,4-regioisomeric nature of the triazoles were in accord with the observation that Cu(I)- and Cu(II)-catalyzed cycloaddition reactions only give the 1,4-substituted triazoles.[8a,9] It was further supported by the observation of triazolyl ring carbon (C-4 and C-5) signals at around δ 148 and 123, respectively, in the ^{13}C NMR spectra, a characteristic of 1,4-substituted triazoles.[19] The structures of all the products were in accord with their spectroscopic data and analysis.

Table 2. Preparation of sugar triazoles **20–24** by the reaction of methyl 5-azido-5-deoxy-2,3-*O*-isopropylidene ribofuranose (**19**) with alkynes **2–6**

Entry no.	Alkyne	Product	Reaction time (h)	Yield (isolated) (%)
1	Phenyl acetylene	**20**	7.5	70
2	Propargyl alcohol	**21**	2.5	87
3	1-Octyne	**22**	10	81
4	1-Heptyne	**23**	9	78
5	3-Phenyl-1-propyne	**24**	9	72

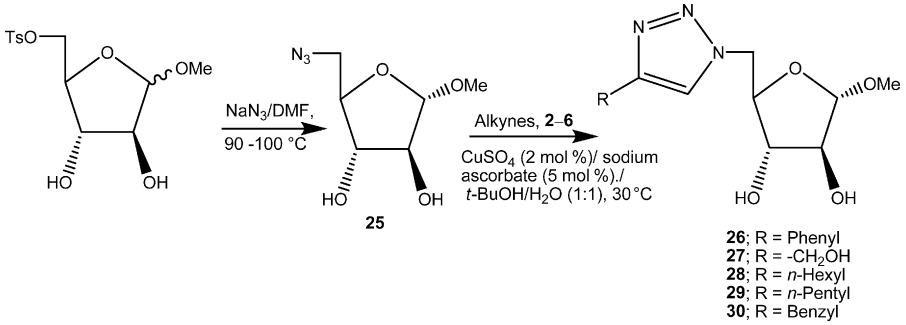
Table 3. Preparation of sugar triazoles **26–30** by the reaction of methyl 5-azido-5-deoxyarabinofuranose (**25**) with alkynes **2–6**

Entry no.	Alkyne	Product	Reaction time (h)	Yield (isolated) (%)
1	Phenyl acetylene	**26**	18	60
2	Propargyl alcohol	**27**	3	80
3	1-Octyne	**28**	16	65
4	1-Heptyne	**29**	14	60
5	3-Phenyl-1-propyne	**30**	10	67

The above-synthesized sugar triazoles **7–11**, **13–15**, **20–24** and **26–30** were evaluated separately against an avirulent strain, *M. tuberculosis H37Ra*, and a virulent strain, *M. tuberculosis H37Rv*. The MIC values were determined using the MABA method[27] and agar microdilution method.[28] As evident from Table 4, among all the compounds screened, none of them were found to possess any significant activity against the avirulent strain. However, one of them, compound **29**, displayed a moderate antitubercular activity with an MIC of 12.5 μg/mL, while other compounds possess MIC values >12.5 μg/mL.

3. Conclusion

A number of sugar azides were prepared by nucleophilic substitution of 5-*O*-*p*-toluenesulfonyl or methansulfonyl glycofuranoses with sodium azide in DMF. The sugar azides were subjected to 1,3-dipolar cycloaddition with different alkynes to give the respective sugar triazoles in excellent yields and with 1,4-regioselectivity. Although the compounds displayed only moderate antitubercular activity, further modifications may lead to



Scheme 3. Synthesis of 4-alkyl/aryl-1-(5-deoxy-α-D-methyl arabinofuranosis-5-yl)-1*H*-1,2,3-triazoles (**26–30**).

Table 4. In vitro antitubercular activities of synthesized sugar triazoles against *M. tuberculosis*[a]

Compound no.	MIC (μg/mL) *M. tuberculosis H37Ra*	MIC (μg/mL) *M. tuberculosis H37Rv*
7	>12.5	>12.5
8	>12.5	>12.5
9	>12.5	>12.5
10	>12.5	>12.5
11	>12.5	>12.5
13	>12.5	>12.5
14	>12.5	>12.5
15	>12.5	>12.5
20	>12.5	>12.5
21	>12.5	>12.5
22	>12.5	>12.5
23	>12.5	>12.5
24	>12.5	>12.5
26	>12.5	>12.5
27	>12.5	>12.5
28	>12.5	>12.5
29	>12.5	12.5
30	>12.5	>12.5

[a] MIC = minimum inhibitory concentration, the lowest concentration of the compound which inhibits the growth of mycobacterium >90%; MIC of the drugs used as control, INH 0.65, rifampicine 0.75, and ethambutol 3.25 μg/mL against *M. tuberculosis H37 Rv*.

more potent anti TB molecules, and such work is currently underway.

4. Experimental

4.1. General methods

Commercially available reagent grade chemicals were used as received. All reactions were followed by TLC on E. Merck Kieselgel 60 F_{254}, with detection by UV light and/or spraying a 5% H_2SO_4 in EtOH. Column chromatography was performed on silica gel (60–120 mesh, E. Merck). IR spectra were recorded as thin films or in chloroform with a Perkin–Elmer Spectrum RX-1 (4000–450 cm^{-1}) spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Brucker DRX-300 in $CDCl_3$. Chemical shift values are reported in ppm relative to $SiMe_4$ as internal reference, unless otherwise stated; s (singlet), d (doublet), t (triplet), m (multiplet); *J* in hertz. MS were performed using a mass Spectrometer Jeol SX-102 and ESIMS were performed using Quattro II (Micromass). HRMS were performed using JEOL MSRoute. Elemental analyses were performed on a Perkin–Elmer 2400 II elemental analyzer. Optical rotations were measured in a 1.0 dm tube with a Rudolf Autopol III polarimeter in $CHCl_3$.

4.2. Preparation of 1-(5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-phenyl-1*H*-1,2,3-triazole (7)

5-Azido-5-deoxy-1,2-*O*-isopropylidne-α-D-xylofuranose (**1**)[17] (1.0 g, 4.7 mmol) and phenylacetylene (0.5 mL, 4.7 mmol) were suspended in a 1:1 mixture of water and *tert*-butyl alcohol (14 mL). Sodium ascorbate (0.05 g, 0.2 mmol, a freshly prepared solution in 500 μL water) was added followed by the addition of $CuSO_4{\cdot}5H_2O$ (0.02 g, 0.09 mmol, freshly prepared solution in 200 μL of water). The heterogeneous mixture was stirred vigorously for 6 h, and the reaction mixture diluted with ice-cold water. The white precipitate thus obtained was collected by filtration and washed with ice-cold water and dried under vacuum to give a crude mass, which was purified by a short column of silica gel (60–120) using 1:2.5 hexane–EtOAc as eluent to give compound **7** as white solid. Yield (1.3 g, 88%); mp 167–168 °C, lit.[16] mp 163–165 °C; $[\alpha]_D$ −71 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3428, 2985, 1596; ^1H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 1.29 (s, 3H, C*H*$_3$ of CMe_2), 1.44 (s, 3H, C*H*$_3$ of CMe_2), 4.33 (dd, 1H, $J = 4.9$ Hz, H-3), 4.51–4.65 (m, 3H, H-4, H-5), 4.74 (d, 1H, $J = 5.1$ Hz, OH), 4.84 (dd, 1H, $J = 5.1$ Hz, H-2), 6.01 (d, 1H, $J = 3.6$ Hz, H-1), 7.33–7.46 (m, 3H, ArH), 7.75–7.80 (m, 2H, ArH), 7.94 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 26.5 (C*Me*$_2$), 27.2 (C*Me*$_2$), 49.5 (C-5), 74.9 (C-2), 79.7 (C-3), 85.8 (C-4), 105.6 (C-1), 112.4 (*C*Me$_2$), 121.7 (C-5 triazole), 126.1 (Ar), 128.8 (Ar), 129.3 (Ar), 130.4 (Ar), 148.2 (C-4 triazole); ESIMS: 318 $(M+H)^+$; HRMS: calcd for $C_{16}H_{19}N_3O_4$ (M^+): 317.1376; found: 317.1368.

4.3. 1-(5-Deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-hydroxymethyl-1*H*-1,2,3-triazole (8)

Compound **8** was obtained by the reaction of **1** (1.0 g, 4.7 mmol) and propargyl alcohol (0.3 mL, 4.7 mmol) as a brown solid: 1.2 g, 97%; mp 85–86 °C; $[\alpha]_D$ −50 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3367, 2365, 1596; ^1H NMR (200 MHz, $CDCl_3$ + DMSO-d_6): δ 1.28 (s, 3H, C*H*$_3$ of CMe_2), 1.41 (s, 3H, C*H*$_3$ of CMe_2), 4.15 (s, 1H, H-3), 4.44–4.67 (m, 4H, H-2, H-4, H-5), 4.72 (s, 2H, CH_2OH), 5.40 (br s, 1H, OH), 5.93 (d, 1H, $J = 3.1$ Hz, H-1), 7.77 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6): δ 26.4 (C*Me*$_2$), 27.0 (C*Me*$_2$), 49.3 (C-5), 56.3 (CH_2OH), 74.3 (C-2), 79.7 (C-3), 85.6 (C-4), 105.3 (C-1), 112.0 (*C*Me$_2$), 123.4 (C-5 triazole), 148.0 (C-4 triazole); ESIMS: 272.1 $(M+H)^+$; HRMS: calcd for $C_{11}H_{17}N_3O_5$ $(M+H)^+$: 272.1246; found: 272.1244.

4.4. 1-(5-Deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-*n*-hexyl-1*H*-1,2,3-triazole (9)

Compound **9** was obtained by the reaction of **1** (0.8 g, 3.8 mmol) and 1-octyne (0.6 mL, 3.8 mmol) as a white solid: 1 g, 82%; mp 80–81 °C; $[\alpha]_D$ −30 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3451, 2924, 1222; ^1H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 0.88 (t, 3H, $J = 6.5$ Hz,

CH_3), 1.31–143 (m, 9H, 3 × CH_2, CH_3 of CMe_2), 1.45 (s, 3H, CH_3 of CMe_2), 1.62–1.65 (m, 2H, CH_2), 2.69 (t, 2H, $J = 7.4$ Hz, CH_2), 4.29 (s, 1H, H-3), 4.47–4.56 (m, 2H, H-5), 4.61 (d, 1H, $J = 3.0$ Hz, H-2), 4.81–4.87 (m, 1H, H-4), 5.10 (s, 1H, OH), 6.0 (d, 1H, $J = 2.9$ Hz, H-1), 7.47 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 14.4 (CH_3), 22.9 (CH_2), 25.9 (CH_2), 26.5 (CMe_2), 27.2 (CMe_2), 29.3 (CH_2), 29.6 (CH_2), 31.9 (CH_2), 49.3 (C-5), 74.8 (C-2), 79.9 (C-3), 85.8 (C-4), 105.6 (C-1), 112.2 (*C*Me_2), 122.6 (C-5 triazole), 148.8 (C-4 triazole); ESIMS: 326.2 $(M+H)^+$; HRMS: calcd for $C_{16}H_{27}N_3O_4$ $(M)^+$: 325.2002; found: 325.2008.

4.5. 1-(5-Deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-*n*-pentyl-1*H*-1,2,3-triazole (10)

Compound **10** was obtained by the reaction of **1** (0.6 g, 2.8 mmol) and 1-heptyne (0.4 mL, 2.8 mmol) as a white solid: 0.72 g, 84%; mp 84–86 °C; $[\alpha]_D$ −25 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3437, 2937, 1220; ^{1}H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 0.90 (t, 3H, $J = 6.2$ Hz, CH_3), 1.25–1.33 (m, 7H, CH_3 of CMe_2, 2 × CH_2), 1.43 (s, 3H, CH_3 of CMe_2), 1.67–1.79 (m, 2H, CH_2), 2.65 (t, 2H, $J = 7.4$ Hz, CH_2), 4.26 (s, 1H, H-3), 4.42–4.48 (m, 2H, H-5), 4.57 (d, 1H, $J = 3.4$ Hz, H-2), 4.84–5.01 (m, 2H, H-4, OH), 5.95 (d, 1H, $J = 3.3$ Hz, H-1), 7.50 (s, 1H, triazolyl H); ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$): δ 12.7 (CH_3), 21.1 (CH_2), 24.1 (CH_2), 24.9 (CH_2), 25.6 (CMe_2), 27.6 (CMe_2), 28.4 (CH_2), 30.1 (CH_2), 48.3 (C-5), 73.0 (C-2), 78.4 (C-3), 84.2 (C-4), 103.9 (C-1), 110.3 (*C*Me_2), 121.5 (C-5 triazole), 147.6 (C-4 triazole); ESIMS: 312.2 $(M+H)^+$; HRMS: calcd for $C_{15}H_{25}N_3O_4$ $(M)^+$: 311.1845; found: 311.1849.

4.6. 4-Benzyl-1-(5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-1*H*-1,2,3-triazole (11)

Compound **11** was obtained by the reaction of **1** (0.5 g, 2.3 mmol) and 3-phenyl-1-propyne (0.3 mL, 2.3 mmol) as a white solid: 0.64 g, 84%; mp 120–122 °C; $[\alpha]_D$ −65 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3452, 3127, 2980, 1217; ^{1}H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 1.28 (s, 3H, CH_3 of CMe_2), 1.42 (s, 3H, CH_3 of CMe_2), 4.03 (s, 2H, CH_2Ph), 4.23 (s, 1H, H-3), 4.38–4.46 (m, 1H, H-4), 4.52 (d, 1H, $J = 3.6$ Hz, H-2), 4.70–4.82 (m, 2H, H-5), 5.91 (d, 1H, $J = 3.5$ Hz, H-1), 7.18–7.30 (m, 5H, ArH), 7.34 (s, 1H, triazolyl H); ^{13}C NMR (75 MHz, $CDCl_3 + CCl_4$): δ 24.9 (CMe_2), 25.6 (CMe_2), 30.7 (CH_2Ph), 48.0 (C-5), 73.0 (C-2), 78.2 (C-3), 84.1 (C-4), 103.8 (C-1), 110.4 (*C*Me_2), 121.8 (C-5 triazole), 125.3 (Ar), 127.3 (Ar), 137.3 (Ar), 137.3 (Ar), 145.9 (C-4 triazole); ESIMS: 332.2 $(M+H)^+$; HRMS: calcd for $C_{17}H_{21}N_3O_4$ $(M)^+$: 331.1532; found: 331.1515.

4.7. 1-(3-*O*-Benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-phenyl-1*H*-1,2,3-triazole (13)

To a stirring slurry of NaH (1.10 g, 46.5 mmol) in anhyd THF (5 mL) at 0 °C, a solution of 5-azido-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**1**) (4.00 g, 18.6 mmol) in THF (20 mL) was added dropwise, followed by the dropwise addition of benzyl chloride (2.30 mL, 20.5 mmol), with stirring continued at ambient temperature overnight to give 5-azido-3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranose (**12**) as a brown oil: 5.2 g, 92%. IR (neat) cm^{-1}: 2987, 2102, 1453, 1078; ^{1}H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 1.28 (s, 3H, CH_3 of CMe_2), 1.46 (s, 3H, CH_3 of CMe_2), 3.43–3.50 (m, 2H, H-5), 3.87 (d, 1H, $J = 3.2$ Hz, H-3), 4.18–4.27 (m, 1H, H-4), 4.45 (d, 1H, $J = 11.7$ Hz, OCH_APh), 4.53 (d, 1H, $J = 3.7$ Hz, H-2), 4.62 (d, 1H, $J = 11.7$ Hz, OCH_BPh), 5.83 (d, 1H, $J = 3.7$ Hz, H-1), 7.24–7.35 (m, 5H, ArH);^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 26.7 (CMe_2), 27.2 (CMe_2), 49.5 (C-5), 72.3 (OCH_2Ph), 79.1 (C-2), 81.9 (C-3), 82.5 (C-4), 105.5 (C-1), 112.2 (*C*Me_2), 128.1 (Ar), 128.4 (Ar), 128.9 (Ar), 137.5 (Ar); ESIMS: 306 $(M+H)^+$.

The reaction of **12** (0.6 g, 1.9 mmol) and phenylacetylene (0.2 mL, 1.9 mmol) and workup of the reaction mixture as in the case of **7** afforded 1-(3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-phenyl-1*H*-1,2,3-triazole (**13**) as a white solid: 0.55 g, 72%; mp 130–131 °C; $[\alpha]_D$ −106 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3130, 2374, 1608; ^{1}H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 1.31 (s, 3H, CH_3 of CMe_2), 1.42 (s, 3H, CH_3 of CMe_2), 3.99 (d, 1H, $J = 2.8$ Hz, H-3), 4.47–4.61 (m, 3H, H-4, OCH_2Ph), 4.65 (d, 1H, $J = 3.8$ Hz, H-2), 4.71–4.78 (m, 2H, H-5), 5.97 (d, 1H, $J = 3.8$ Hz, H-1), 7.30–7.44 (m, 8H, ArH), 7.76–7.81 (m, 3H, ArH, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 25.0 (CMe_2), 25.5 (CMe_2), 47.9 (C-5), 70.7 (OCH_2Ph), 77.6 (C-2), 80.4 (C-3), 80.7 (C-4), 103.9 (C-1), 110.8 (*C*Me_2), 119.3 (C-5 triazole), 124.4 (Ar), 126.6 (Ar), 127.0 (Ar), 127.4 (Ar), 129.3 (Ar), 135.5 (Ar), 146.4 (C-4 triazole); ESIMS: 408.3 $(M+H)^+$; HRMS: calcd for $C_{23}H_{25}N_3O_4$ $(M)^+$: 407.1845; found: 407.1832.

4.8. 1-(3-*O*-Benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-hydroxymethyl-1*H*-1,2,3-triazole (14)

Compound **14** was obtained by the reaction of **12** (0.56 g, 1.8 mmol) and propargyl alcohol (0.1 mL, 1.8 mmol) as a brown solid: 0.62 g, 94%; mp 119–120 °C; $[\alpha]_D$ −75 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3319, 2914, 1649; ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.29 (s, 3H, CH_3 of CMe_2), 1.41 (s, 3H, CH_3 of CMe_2), 2.87 (br s, 1H, OH), 3.96 (d, 1H, $J = 2.8$ Hz, H-3), 4.45–4.55 (m, 3H, H-4, H-5), 4.59–4.75 (m, 5H, H-2, CH_2OH,

OCH_2Ph), 5.93 (d, 1H, $J = 3.7$ Hz, H-1), 7.33–7.36 (m, 5H, ArH), 7.53 (s, 1H, triazolyl H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 24.9 (CMe_2), 25.5 (CMe_2), 47.7 (C-5), 54.8 (CH_2OH), 70.7 (OCH_2Ph), 77.5 (C-2), 80.3 (C-3), 80.7 (C-4), 103.8 (C-1), 110.7 (CMe_2), 121.4 (C-5 triazole), 126.6 (Ar), 127.0 (Ar), 127.3 (Ar), 135.5 (Ar), 146.6 (C-4 triazole); ESIMS: 362.3 $(M+H)^+$; HRMS: calcd for $C_{18}H_{24}N_3O_5$ $(M+H)^+$: 362.1716; found: 362.1714.

4.9. 1-(3-*O*-Benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-*n*-hexyl-1*H*-1,2,3-triazole (15)

Compound **15** was obtained by the reaction of **12** (0.7 g, 2.3 mmol) with 1-octyne (0.4 mL, 2.3 mmol) as a colourless solid: 0.79 g, 82%; mp 68–69 °C; $[\alpha]_D$ −63 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3068, 2926, 1458; ^1H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 0.88 (t, 3H, $J = 6.6$ Hz, CH_3), 1.29–1.38 (m, 9H, $3 \times CH_2$, CH_3 of CMe_2), 1.41 (s, 3H, CH_3 of CMe_2) 1.61–1.64 (m, 2H, CH_2), 2.66 (t, 2H, $J = 7.6$ Hz, CH_2), 3.94 (d, 1H, $J = 2.2$ Hz, H-3), 4.43–4.57 (m, 3H, H-4, H-5), 4.62–4.75 (m, 3H, H-2, OCH_2Ph), 5.93 (d, 1H, $J = 3.7$ Hz, H-1), 7.27–7.33 (m, 6H, ArH, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 14.5 (CH_3), 22.9 (CH_2), 26.0 (CH_2), 26.6 (CMe_2), 27.1 (CMe_2), 29.3 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 49.2 (C-5), 72.3 (OCH_2Ph), 79.3 (C-2), 82.0 (C-3), 82.3 (C-4), 105.5 (C-1), 112.3 (CMe_2), 121.8 (C-5 triazole), 128.2 (Ar), 128.6 (Ar), 129.0 (Ar), 137.2 (Ar), 148.6 (C-4 triazole); ESIMS: 416.4 $(M+H)^+$; Anal. Calcd for $C_{23}H_{33}N_3O_4$ C, 66.48; H, 8.00; N, 10.11. Found: C, 66.39; H, 8.11; N, 10.16.

4.10. 1-(3-*O*-Benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-4-*n*-pentyl-1*H*-1,2,3-triazole (16)

Compound **16** was obtained by the reaction of **12** (0.3 g, 1.1 mmol) and 1-heptyne (0.14 mL, 1.1 mmol) as an oil: 0.38 g, 90%; $[\alpha]_D$ −78 (*c* 0.1, $CHCl_3$); IR (neat) cm^{-1}: 2930, 2364, 1457, 1217; ^1H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 0.89 (t, 3H, $J = 6.3$ Hz, CH_3), 1.25–1.36 (m, 7H, $2 \times CH_2$, CH_3 of CMe_2). 1.42 (s, 3H, CH_3 of CMe_2), 1.61–1.69 (m, 2H, CH_2), 2.66 (t, 2H, $J = 8.0$ Hz, CH_2), 3.95 (d, 1H, $J = 2.6$ Hz, H-3), 4.43–4.51 (m, 3H, H-4, H-5), 4.57–4.75 (m, 3H, H-2, OCH_2Ph), 5.93 (d, 1H, $J = 3.7$ Hz, H-1), 7.27–7.38 (m, 6H, ArH, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 14.4 (CH_3), 22.8 (CH_2), 26.0 (CH_2), 26.6 (CMe_2), 27.1 (CMe_2), 29.4 (CH_2), 31.8 (CH_2), 49.2 (C-5), 72.4 (OCH_2Ph), 79.3 (C-2), 82.0 (C-3), 82.3 (C-4), 105.5 (C-1), 112.3 (CMe_2), 121.9 (C-5 triazole), 128.2 (Ar), 128.6 (Ar), 129.0 (Ar), 137.2 (Ar), 148.6 (C-4 triazole); ESIMS: 402.3 $(M+H)^+$; HRMS: calcd for $C_{22}H_{30}N_3O_4$ $(M-H)^+$: 400.2236; found: 400.2226.

4.11. 4-Benzyl-1-(3-*O*-benzyl-5-deoxy-1,2-*O*-isopropylidene-α-D-xylofuranos-5-yl)-1*H*-1,2,3-triazole (17)

Compound **17** was obtained by the reaction of **12** (0.3 g, 1 mmol) and 3-phenyl-1-propyne (0.13 mL, 1 mmol) as a white solid: 0.41 g, 91%; mp 81–82 °C; $[\alpha]_D$ −86 (*c* 0.1, $CHCl_3$); IR (neat) cm^{-1}: 2925, 2361, 1647, 752; ^1H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 1.28 (s, 3H, CH_3 of CMe_2), 1.41 (s, 3H, CH_3 of CMe_2), 3.90 (d, 1H, $J = 2.5$ Hz, H-3), 4.03 (d, 2H, $J = 4.2$ Hz, CH_2Ph), 4.37–4.61 (m, 6H, H-4, H-5, H-2, OCH_2Ph), 5.90 (d, 1H, $J = 3.7$ Hz, H-1), 7.17–7.34 (m, 11H, ArH, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 26.6 (CMe_2), 27.2 (CMe_2), 32.6 (CH_2Ph), 49.2 (C-5), 72.4 (OCH_2Ph), 79.2 (C-2), 82.0 (C-3), 82.3 (C-4), 105.5 (C-1), 112.4 (CMe_2), 122.8 (C-5 triazole), 126.8 (Ar), 128.2 (Ar), 128.6 (Ar), 128.9 (Ar), 129.0 (Ar), 129.1 (Ar), 137.2 (Ar), 139.5 (Ar), 147.7 (C-4 triazole); ESIMS: 422.3 $(M+H)^+$; HRMS: calcd for $C_{24}H_{27}N_3O_4$ $(M)^+$: 421.2002; found: 421.2008.

4.12. 1-(Methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranosid-5-yl)-4-phenyl-1*H*-1,2,3-triazole (20)

Compound **20** was obtained by the reaction of **19** (0.5 g, 2.2 mmol) and phenylacetylene (0.24 mL, 2.20 mmol) as a colourless solid: 0.54 g, 70%; mp 134–135 °C, lit.[16] mp 135–136 °C; $[\alpha]_D$ −34 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3086, 2944, 1655; ^1H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 1.30 (s, 3H, CH_3 of CMe_2), 1.45 (s, 3H, CH_3 of CMe_2), 3.41 (s, 3H, OCH_3), 4.44–4.63 (m, 3H, H-4, H-5), 4.65 (d, 1H, $J = 5.9$ Hz, H-3), 4.75 (d, 1H, $J = 5.9$ Hz, H-2), 5.01 (s, 1H, H-1), 7.31–7.44 (m, 3H, ArH), 7.80–7.85 (m, 3H, ArH, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 25.3 (CMe_2), 26.8 (CMe_2), 53.4 (C-5), 55.9 (OCH_3), 82.1 (C-2), 85.3(C-3), 85.5 (C-4), 110.4 (C-1), 113.2 (CMe_2), 120.0 (C-5 triazole), 126.1 (Ar), 128.5 (Ar), 129.1 (Ar), 130.9 (Ar), 148.3 (C-4 triazole); ESIMS: 332 $(M+H)^+$; HRMS: calcd for $C_{16}H_{18}N_3O_4$ $(M-CH_3)^+$: 316.1297; found: 316.1295.

4.13. 4-Hydroxymethyl-1-(methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranosid-5-yl)-1*H*-1,2,3-triazole (21)

Compound **21** was obtained by the reaction of **19** (3.70 g, 16.2 mmol) and propargyl alcohol (1.10 mL, 16.2 mmol) as a brown solid: 4 g, 87%; $[\alpha]_D$ −36 (*c* 0.1, $CHCl_3$); mp 81–82 °C; IR (KBr) cm^{-1}: 3462, 2985, 1653; ^1H NMR (200 MHz, $CDCl_3$): δ 1.30 (s, 3H, CH_3 of CMe_2), 1.45 (s, 3H, CH_3 of CMe_2), 3.38 (s, 3H, OCH_3), 4.40–4.59 (m, 5H, H-4, H-5, CH_2OH), 4.65 (d, 1H, $J = 5.9$ Hz, H-3), 4.74 (d, 1H, $J = 6.2$ Hz, H-2), 5.01 (s, 1H, H-1), 7.68 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 25.3 (CMe_2), 26.7 (CMe_2), 53.5 (C-5), 55.9 (OCH_3), 56.6 (CH_2OH), 82.1 (C-2), 85.3 (C-3), 85.5 (C-4), 110.4 (C-1), 113.3 (CMe_2), 122.5

(C-5 triazole), 148.0 (C-4 triazole); ESIMS: 286 $(M+H)^+$; Anal. Calcd For $C_{12}H_{19}N_3O_5$: C, 50.52; H, 6.71; N, 14.73. Found: C, 50.65; H, 6.60; N, 14.80.

4.14. 4-*n*-Hexyl-1-(methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranosid-5-yl)-1*H*-1,2,3-triazole (22)

Compound **22** was obtained by the reaction of **19** (0.5 g, 2.2 mmol) and 1-octyne (0.3 mL, 2.2 mmol) as a white solid: 0.6 g, 81%; mp 50–51 °C; $[\alpha]_D$ −45 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3086, 2944, 1655; ^1H NMR (300 MHz, $CDCl_3 + CCl_4$): δ 0.90 (t, 3H, $J = 6.5$ Hz, CH_3), 1.24–1.46 (m, 9H, CH_3 of CMe_2, 3 × CH_2), 1.51 (s, 3H, CH_3 of CMe_2), 1.63–1.73 (m, 2H, CH_2), 2.72 (t, 2H, $J = 7.6$ Hz, CH_2), 3.39 (s, 3H, OCH_3), 4.32–4.42 (m, 1H, H-4), 4.48–4.56 (m, 2H, H-5), 4.63 (d, 1H, $J = 5.9$ Hz, H-3), 4.72 (d, 1H, $J = 5.9$ Hz, H-2), 4.99 (s, 1H, H-1), 7.34 (s, 1H, triazolyl *H*); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 14.5 (CH_3), 22.9 (CH_2), 25.3 (C*Me*$_2$), 26.0 (CH_2), 26.8 (C*Me*$_2$), 29.3 (CH_2), 29.7 (CH_2), 31.9 (CH_2), 53.1 (C-5), 55.7 (OCH_3), 82.1 (C-2), 85.3 (C-3), 85.5 (C-4), 110.3 (C-1), 113.0 (*C*Me_2), 120.8 (C-5 triazole), 148.7 (C-4 triazole); ESIMS: 340.1 $(M+H)^+$; HRMS: calcd for $C_{17}H_{29}N_3O_4$ $(M)^+$: 339.2158; found: 339.2137.

4.15. 1-(Methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranosid-5-yl)-4-*n*-pentyl-1*H*-1,2,3-triazole (23)

Compound **23** was obtained by the reaction of **19** (0.5 g, 2.2 mmol) and 1-heptyne (0.3 mL, 2.2 mmol) as an oil: 0.55 g, 78%; $[\alpha]_D$ −70 (*c* 0.18, $CHCl_3$); IR (neat) cm^{-1}: 2933, 1651, 1377; ^1H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 0.90 (t, 3H, $J = 6.8$ Hz, CH_3), 1.29–1.39 (m, 7H, CH_3 of CMe_2, 2 × CH_2), 1.45 (s, 3H, CH_3 of CMe_2), 1.64–1.76 (m, 2H, CH_2), 2.70 (d, 2H, $J = 7.9$ Hz, CH_2), 3.38 (s, 3H, OCH_3), 4.35–4.55 (m, 3H, H-4, H-5), 4.63 (d, 1H, $J = 5.9$ Hz, H-3), 4.71 (d, 1H, $J = 5.9$ Hz, H-2), 4.99 (s, 1H, H-1), 7.35 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 14.4 (CH_3), 22.7 (CH_2), 25.3 (C*Me*$_2$), 26.0 (CH_2), 26.7 (C*Me*$_2$), 29.4 (CH_2), 31.8 (CH_2), 53.2 (C-5), 55.7 (OCH_3), 82.1 (C-2), 85.3 (C-3), 85.5 (C-4), 110.3 (C-1), 113.1 (*C*Me_2), 120.9 (C-5 triazole), 148.8 (C-4 triazole); ESIMS: 326.1 $(M+H)^+$; HRMS: calcd for $C_{16}H_{28}N_3O_4$ $(M+H)^+$: 326.2080; found: 326.2067.

4.16. 4-Benzyl-1-(methyl 5-deoxy-2,3-*O*-isopropylidene-β-D-ribofuranosid-5-yl)-1*H*-1,2,3-triazole (24)

Compound **24** was obtained by the reaction of **19** (0.4 g, 1.7 mmol) and 3-phenyl-1-propyne (0.2 mL, 1.7 mmol) as a white solid: 0.43 g, 72%; mp 60–61 °C; $[\alpha]_D$ −44 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3129, 2943, 1380, 1215; ^1H NMR (200 MHz, $CDCl_3 + CCl_4$): δ 1.28 (s, 3H, CH_3 of CMe_2), 1.43 (s, 3H, CH_3 of CMe_2), 3.32 (s, 3H, OCH_3), 4.08 (s, 2H, CH_2Ph), 4.30–4.51 (m, 3H, H-4, H-5), 4.60 (d, 1H, $J = 5.9$ Hz, H-3), 4.70 (d, 1H, $J = 5.9$ Hz, H-2), 4.95 (s, 1H, H-1), 7.20–7.29 (m, 6H, ArH, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3 + CCl_4$): δ 25.3 (C*Me*$_2$), 26.8 (C*Me*$_2$), 32.6 (CH_2Ar), 53.2 (C-5), 55.7 (OCH_3), 82.1 (C-2), 85.3 (C-3), 85.5 (C-4), 110.4 (C-1), 113.1 (*C*Me_2), 121.9 (C-5 triazole), 126.8 (Ar), 128.9 (Ar), 129.1 (Ar), 139.3 (Ar), 148.1 (C-4 triazole); ESIMS: 346.1 $(M+H)^+$; HRMS: calcd for $C_{17}H_{21}N_3O_4$ $(M)^+$: 345.1689; found: 345.1689.

4.17. 1-(Methyl 5-deoxy-α-D-arabinofuranosid-5-yl)-4-phenyl-1*H*-1,2,3-triazole (26)

Compound **26** was obtained by the reaction of **25** (0.46 g, 2.40 mmol) and phenylacetylene (0.3 mL, 2.4 mmol) as a colourless oil: 0.42 g, 60%; $[\alpha]_D$ +81 (*c* 0.1, $CHCl_3$); IR (neat) cm^{-1}: 3397, 2927, 2370, 1653, 1100; ^1H NMR (200 MHz, $CDCl_3$) δ 3.23 (s, 3H, OCH_3), 3.87 (s, 1H, H-3), 4.13 (s, 1H, H-2), 4.25 (d, 1H, $J = 4.2$ Hz, H-4), 4.50–4.67 (m, 2H, H-5), 4.79 (s, 1H, H-1), 5.1 (br s, 1H, OH), 7.18–7.32 (m, 3H, ArH), 7.63–7.64 (m, 2H, ArH), 7.86 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 52.1 (C-5), 55.5 (OCH_3), 78.5 (C-2), 80.0 (C-3), 81.9 (C-4), 109.4 (C-1), 122.2 (C-5 triazole), 126.0 (Ar), 128.6 (Ar), 129.2 (Ar), 130.4 (Ar), 147.9 (C-4 triazole); ESIMS: 292.2 $(M+H)^+$; HRMS: calcd for $C_{14}H_{17}N_3O_4$ $(M)^+$: 291.1219; found: 291.1223.

4.18. 4-Hydroxymethyl-1-(methyl 5-deoxy-α-D-arabinofuranosid-5-yl)-1*H*-1,2,3-triazole (27)

Compound **27** was obtained by the reaction of **25** (0.7 g, 3.8 mmol) and propargyl alcohol (0.2 mL, 3.8 mmol) as a colourless oil: 0.74 g, 80%; $[\alpha]_D$ +31 (*c* 0.1, $CHCl_3$); IR (neat) cm^{-1}: 3430, 2926, 2373, 1627, 1171, 1028; ^1H NMR (200 MHz, $CDCl_3$ + DMSO-d_6) δ 3.35 (s, 3H, OCH_3), 3.58–3.62 (m, 1H, H-3), 3.95 (s, 1H, H-2), 4.20–4.23 (m, 1H, H-4), 4.58–4.66 (m, 4H, H-5, CH_2OH), 4.75 (s, 1H, H-1), 5.23 (br s, 1H), 7.76 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3$ + DMSO-d_6) δ 51.6 (C-5), 55.4 (OCH_3), 55.8 (CH_2OH), 78.0 (C-2), 81.7 (C-3), 82.0 (C-4), 109.3 (C-1), 124.3 (C-5 triazole), 148.0 (C-4 triazole); ESIMS: 246.2 $(M+H)^+$. Anal. Calcd For $C_9H_{15}N_3O_5 \cdot 2H_2O$: C, 38.43; H, 6.76; N, 14.94. Found: C, 38.24; H, 6.80; N, 14.62.

4.19. 4-*n*-Hexyl-1-(methyl 5-deoxy-α-D-arabinofuranosid-5-yl)-1*H*-1,2,3-triazole (28)

Compound **28** was obtained by the reaction of **25** (0.53 g, 2.8 mmol) and 1-octyne (0.4 mL, 2.8 mmol) as a colourless oil: 0.54 g, 65%; $[\alpha]_D$ +64 (*c* 0.1, $CHCl_3$); IR (neat) cm^{-1}: 3425, 2927, 2371, 1656, 1103; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3H, $J = 6.3$ Hz, CH_3),

1.25–1.40 (m, 6H, 3 × CH_2), 1.61–1.65 (m, 2H, CH_2), 2.64 (t, 2H, $J = 7.8$ Hz, CH_2), 3.34 (s, 3H, OCH_3), 3.70–3.75 (m, 1H, H-3), 4.08 (s, 1H, H-2), 4.21–4.61 (m, 3H, H-4, H-5), 4.77 (s, 1H, H-1), 7.46 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.4 (CH_3), 22.9 (CH_2), 25.8 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 31.9 (CH_2), 51.7 (C-5), 55.5 (OCH_3), 78.3 (C-2), 81.6 (C-3), 82.0 (C-4), 109.5 (C-1), 123.1 (C-5 triazole), 148.5 (C-5 triazole); ESIMS: 300 $(M+H)^+$; HRMS: calcd for $C_{14}H_{25}N_3O_4$ $(M)^+$: 299.1845; found: 299.1812.

4.20. 1-(Methyl 5-deoxy-α-D-arabinofuranosid-5-yl)-4-*n*-pentyl-1*H*-1,2,3-triazole (29)

Compound **29** was obtained by the reaction of **25** (0.56 g, 3.0 mmol) and 1-heptyne (0.4 mL, 3.0 mmol) as a colourless oil: 0.50 g, 60%; $[\alpha]_D$ +58 (*c* 0.1, $CHCl_3$); IR (neat) cm^{-1}: 3443, 2927, 2271, 1632, 1105, 1034; ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, 3H, $J = 6.3$ Hz, CH_3), 1.26–1.33 (m, 4H, 2 × CH_2), 1.57–1.64 (m, 2H, CH_2), 2.62 (t, 2H $J = 7.8$ Hz, CH_2), 3.30 (s, 3H, OCH_3), 3.74 (d, 1H, $J = 3.4$ Hz, H-3), 4.06 (s, 1H, H-2), 4.18–4.23 (m, 1H, H-4), 4.55–4.58 (m, 2H, H-5), 4.75 (s, 1H, H-1), 5.1 (br s, 2H, 2 × OH), 7.47 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.4 (CH_3), 22.7 (CH_2), 25.7 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 51.8 (C-5), 55.3 (OCH_3), 78.5 (C-2), 81.7 (C-3), 81.9 (C-4), 109.5 (C-1), 123.0 (C-5 triazole), 148.3 (C-4 triazole); ESIMS: 286.2 $(M+H)^+$; HRMS: calcd for $C_{13}H_{23}N_3O_4$ $(M)^+$: 285.1689; found: 285.1682.

4.21. 4-Benzyl-1-(methyl 5-deoxy-α-D-arabinofuranosid-5-yl)-1*H*-1,2,3-triazole (30)

Compound **30** was obtained by the reaction of **25** (0.5 g, 2.6 mmol) and 3-phenyl-1-propyne (0.3 mL, 2.6 mmol) as a white solid: 0.54 g, 67%; mp 88–89 °C; $[\alpha]_D$ +85 (*c* 0.1, $CHCl_3$); IR (KBr) cm^{-1}: 3129, 2943, 1380, 1215; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.31 (s, 3H, OCH_3), 3.73 (dd, 1H, $J = 3.5$ Hz each, H-3), 4.02 (s, 2H, CH_2Ph), 4.09–4.24 (m, 2H, H-4, H-2), 4.48–4.55 (m, 2H, H-5), 4.75 (s, 1H, H-1), 4.88 (s, 1H, OH), 7.18–7.30 (m, 5H, ArH), 7.37 (s, 1H, triazolyl H); ^{13}C NMR (50 MHz, $CDCl_3$): δ 32.3 (CH_2), 51.7 (C-5), 55.6 (OCH_3), 78.3 (C-2), 81.8 (C-3), 81.9 (C-4), 109.4 (C-1), 124.1 (C-4 triazole), 126.9 (Ar), 129.0 (Ar), 139.0 (Ar), 147.8(C-4 triazole); ESIMS: 306.2 $(M+H)^+$; HRMS: calcd for $C_{15}H_{19}N_3O_4$ $(M)^+$: 305.1376; found: 305.1303.

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Supplementary data

HRMS, ESIMS, ^{1}H NMR and ^{13}C NMR spectra of all the new compounds are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.02.013.

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