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Novel Lipase-Catalysed Highly Selective Acetylation Studies on D-*Arabino*- and D-*Threo*-polyhydroxyalkyltriazoles†

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Abstract—Capabilities of lipases from *Candida antarctica, Candida rugosa* and porcine pancreas have been evaluated for regioselective acetylation of 2-phenyl-4-(D-*arabino*-tetrahydroxybutyl)-2*H*-1,2,3-triazole, 2-phenyl-4-(D-*arabino*-*O*-1′,2′-*iso*propylidene-3′,4′-dihydroxybutyl)-2*H*-1,2,3-triazole and 2-phenyl-4-(D-*threo*-trihydroxypropyl)-2*H*-1,2,3-triazole, precursors for the synthesis of triazolylacyclonucleosides. *C. antarctica* lipase and porcine pancreatic lipase exhibited exclusive selectivity for the acetylation of primary hydroxyl group over secondary hydroxyl group(s) in all the three cases.

Introduction

The control of regiochemistry and stereochemistry during the course of chemical transformations is a great challenge for the synthetic organic chemist. For example, selective manipulation of hydroxyl groups in polyhydroxy compounds is always required when sugars, polyols or polyphenolics are used as starting materials.[1–5] Among the different polyhydroxy compounds, carbohydrates have always been a focal point because of their chiral pool characteristics.[6] In the recent past, a plethora of work has been done in the area of modification of sugars towards the synthesis of sugar modified nucleosides and nucleotides in search of antiviral candidates, for example AZT, ddc, d4T, and so on and in antisense and antigene strategies for selective regulation of gene expression.[7–10] Synthesis of these highly functionalised bioactive molecules containing modified sugar moieties requires multi-step protocols involving protections and deprotections of hydroxyl groups which result in overall low yields.[11,12]

Recently, enzymes have emerged as economical and environment-friendly catalysts to carry out highly regio-, chemo- and stereoselective reactions. We have also demonstrated the capabilities of lipases from *Candida antarctica* and *Pseudomonas* sp for regioselective acylation of hydroxyl groups in 2-deoxy-D-ribose and D-ribose,[13] and for the acylation of one out of the two similar hydroxymethyl groups present in some 4-*C*-hydroxymethyl-1,2-*O*-*iso*propylidene-α-D-pentofuranose derivatives,[14,15] key intermediates for the synthesis of bicyclonucleosides.[16,17] We herein wish to report lipase-catalysed highly selective acetylation of hydroxyl groups present in 2-phenyl-4-(D-*arabino*-1′,2′,3′,4′-tetrahydroxybutyl)-2*H*-1,2,3-triazole (**1**), 2-phenyl-4-(D-*arabino*-*O*-1′,2′-*iso*propylidene-3′,4′-dihydroxybutyl)-2*H*-1,2,3-triazole (**3**) and 2-phenyl-4-(D-*threo*-1′,2′,3′-trihydroxypropyl)-2*H*-1,2,3-triazole (**5**) using vinyl acetate as acetylating agent in organic solvents.

Results and Discussion

Synthesis

The triazolyl sugar **1** was prepared in two steps starting from glucose via its conversion into phenylosazone, followed by oxidative cyclisation of the osazone with 1% $CuSO_4$ in an overall yield of 43% (Scheme 1).[18] The conversion of tetrahydroxybutyltriazole **1** to its di-*iso*-

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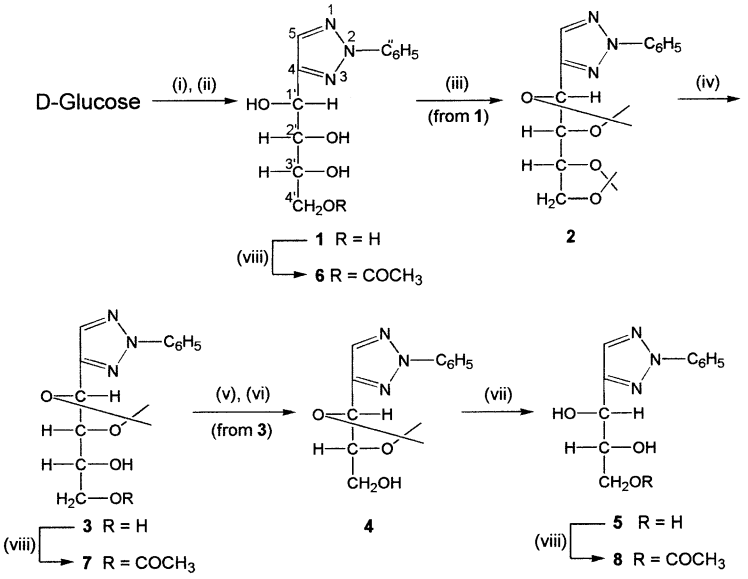
propylidene derivative **2** by acetone–anhydrous ferric chloride method,[19] followed by the selective deprotection of 3′,4′-*O*- *iso*propylidene function led to the formation of 1′,2′-*O*-*iso*propylidene-3′,4′-dihydroxybutyltriazole **3** in 68% yield (Scheme 1). The $NaIO_4$ oxidation, followed by $NaBH_4$ reduction[20] of mono-*iso*propylidine derivative **3** lead to the formation of 2-phenyl-4-(D-*threo*-*O*-1′,2′-*iso*propylidene-3′-hydroxypropyl)-2*H*-1,2,3-triazole **4**, which on deprotection of *iso*propylidene protection afforded *threo*-trihydroxypropyltriazole **5** in 60% yield (Scheme 1). The structures of all the five compounds **1**–**5**, prepared in our laboratory under a programme of synthesis of triazolylacyclonucleosides for antiviral activity evaluation, were unambiguously established on the basis of their spectral analysis. The melting points of two known compounds, that is, triazolyl sugars **1** and **5** were found identical with those reported in the literature,[18,21] however the complete spectral data for triazolyl sugars **1** and **5** is being reported here for the first time.

Regioselective enzymatic acetylation

Different lipases, that is *C. antarctica* lipase (CAL) and *Candida rugosa* lipase (CRL) in diisopropyl ether (DIPE), and porcine pancreatic lipase (PPL) in tetrahydrofuran (THF) were screened for the selective acetylation of hydroxyl groups in tetra-, di- and trihydroxylated triazolyl sugars **1**, **3** and **5**. The selection of solvent for different lipases was done on the basis of our earlier experience.[4] No appreciable conversion was observed in the case of acetylation of compounds **1**, **3** or **5** catalysed by CRL in DIPE even after 34 h of incubation at 42–45 °C. Further, the rate of acetylation of triazolyl sugars **1**, **3** and **5** catalysed by PPL in THF was very slow with respect to the acetylation catalysed by CAL in DIPE (Table 1).

In a typical reaction, a solution of the triazolyl sugar (**1**, **3** or **5**, 1 mmol) and vinyl acetate (4.4 mmol) in DIPE/THF (20 mL) was incubated with CAL/PPL (150 mg) in an incubator shaker at 42–45 °C and the progress of the reaction was monitored by HPLC and/or TLC. On completion of the reaction, enzyme was filtered off and solvent removed under reduced pressure to obtain the crude product, which on purification by column chromatography afforded the acetylated product and the unreacted starting compound. It was observed that both CAL and PPL exclusively acetylate the primary hydroxyl group over the secondary hydroxyl group(s) in all the three triazolyl sugars **1**, **3** and **5** leading to the formation of 2-phenyl-4-(D-*arabino*-4′-acetoxy-1′,2′,3′-trihydroxy-butyl)-2*H*-1,2,3-triazole (**6**), 2-phenyl-4-(D-*arabino*-4′-acetoxy-*O*-1′,2′-*iso*propylidene-3′-hydroxybutyl)-2*H*-1,2,3-triazole (**7**) and 2-phenyl-4-(D-*threo*-3′-acetoxy-1′,2′-dihydroxypropyl)-2*H*-1,2,3-triazole (**8**), respectively. All the three partially acetylated compounds **6**–**8** are new in literature and have been fully characterised on the basis of their spectral data. As indicated during screening, the rate of acetylation of primary hydroxyl groups of triazolyl sugars **1**, **3** and **5** catalysed by CAL in DIPE was much faster as compared to the rate of acetylation catalysed by PPL in THF. Thus, acetylation of triazolyl sugar **1** to monoacetate **6** catalysed by CAL in DIPE was completed in 2 h, whereas the conversion was only 72% even after 26 h of incubation of **1** with PPL in THF. Similar trends were observed for the other two triazolyl sugars **3** and **5** (Table 1). The acetylation reaction catalysed by PPL practically stops after 68–76% conversion of the starting compounds **1**, **3** and **5** into the monoacetylated products **6**, **7** and **8**; both the lipases exclusively acetylate the primary hydroxyl group in these compounds. It is interesting to note that the rate of acetylation of the primary hydroxyl group catalysed by CAL in DIPE increases as the number of hydroxyl group in the substrate increases. Thus, the rate of acetylation of tetrahydroxybutyltriazole **1** catalysed by CAL in DIPE was 4 and 1.75 times faster than the rate of acetylation of



Scheme 1. Reagents and conditions: (i) $PhNHNH_2$, acetic acid, H_2O, reflux; (iii) 1% aq $CuSO_4 \bullet 5H_2O$ solution, H_2O, reflux; (iii) $FeCl_3$, acetone, stirring, 25–28 °C; (iv) 80% acetic acid, stirring, 25–28 °C; (v) $NaIO_4$, H_2O/dioxane (1:1), stirring, 25–28 °C; (vi) $NaBH_4$, H_2O/dioxane (1:1) ethanol, stirring, 25–28 °C; (vii) 80% acetic acid, reflux; (viii) CAL-DIPE/PPL-THF, vinyl acetate, 42–45 °C.

Table 1. Regioselective acetylation of triazolyl sugars **1**, **3** and **5** mediated by lipases at 42–45°C using vinyl acetate as acylating agent[a]

Substrate	Lipase-solvent (RT in h)	Product	% Yield in case of reaction with CAL-DIPE/PPL-THF
2-Phenyl-4-(D-*arabino*-1′,2′,3′,4′-tetrahydroxybutyl)-2*H*-1,2,3-triazole (**1**)	CAL-DIPE/PPL-THF (2/26)	2-Phenyl-4-(D-*arabino*-4′-acetoxy-1′,2′,3′-trihydroxybutyl)-2*H*-1,2,3-triazole (**6**)	98/72
2-Phenyl-4-(D-*arabino*-*O*-1′,2′-*iso*propylidene-3′,4′-dihydroxybutyl)-2*H*-1,2,3-triazole (**3**)	CAL-DIPE/PPL-THF (8/72)	2-Phenyl-4-(D-*arabino*-4′-acetoxy-*O*-1′,2′-*iso*-propylidene-3′-hydroxybutyl)-2*H*-1,2,3- triazole (**7**)	95/76
2-Phenyl-4-(D-*threo*-1′,2′,3′-trihydroxypropyl)-2*H*-1,2,3-triazole (**5**)	CAL-DIPE/PPL-THF (3.5/48)	2-Phenyl-4-(D-*threo*-3′-acetoxy-1′,2′-dihydroxypropyl)-2*H*-1,2,3-triazole (**8**)	97/68

[a]All these reactions when performed under identical conditions but without addition of the enzyme did not yield any product.

dihydroxybutyltriazole **3** and trihydroxypropyltriazole 5, respectively (Table 1). This indicates that the interaction of the secondary hydroxyl groups with the active site of the enzyme facilitates the acetylation of the primary hydroxyl group present in the substrate. This is the first report of enzyme-catalysed selective acetylation studies on triazolyl sugars.

Conclusion

The above study has revealed that CAL in DIPE exhibits exclusive selectivity for the acetylation of primary hydroxyl group over secondary hydroxyl group(s) in triazolyl sugars. The turn over of the acetylation reaction was very high and 95–98% conversion was observed in 2–8 h. The enzymatic method developed for the selective acetylation of primary hydroxyl group in triazolyl sugars may offer a significant advantage over the chemical methods for selective manipulation of different hydroxyl groups en route to multistep synthesis of bioactive molecules of this class. All these reactions when performed under identical conditions but without addition of the enzyme did not yield any product.

Experimental

General

Melting points were determined on a Mettler FP62 instrument and are uncorrected. The IR spectra were recorded either on a Perkin-Elmer model 2000 FT-IR or RXI FT-IR spectrometer. The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AC-300 spectrometer at 300 and at 75.5 MHz, respectively using TMS as internal standard. The chemical shift values are on δ scale and the coupling constants (*J*) are in Hz. The EIMS were recorded on a Jeol AX 505 W instrument at 70 eV. The *C. antarctica* lipase immobilised on accurel was gifted by Novo Nordisk Co. and used as such. The enzymes, porcine pancreatic lipase (PPL, Type II) and *C. rugosa* lipase (CRL, Type VII) were purchased from Sigma Chemical Co. (USA) and used after storing in vacuo over P_2O_5 for 24 h. The organic solvents (THF and DIPE) used were distilled over activated molecular sieves (4 Å). Analytical TLCs were performed on pre-coated Merck silica gel $60F_{254}$ plates; the spots were detected either by UV light or by charring with 4% alcoholic H_2SO_4. Reactions were monitored at λ_{254} nm on a Shimadzu LC-10AS HPLC instrument with SPD-10A UV–Vis detector and Shimpack CLC-ODS (4.6×150 mm) reverse phase column; solvent system used was methanol–water (3:2) at a flow rate of 0.50 mL/min.

2-Phenyl-4-(D-*arabino*-1′,2′,3′,4′-tetrahydroxybutyl)-2H-1,2,3-triazole (1). The tetrahydroxybutyltriazole **1** was prepared from glucose phenylosazone by the method of Hann and Hudson,[18] it was obtained as a white crystalline solid in 54% yield, mp 194–195 °C (lit.[21] mp 195–196 °C). R_f 0.28 (chloroform–methanol, 9:1); IR (Nujol): 3287 (OH), 2923, 2360, 1596, 1462, 1377, 1089 and 968 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-d_6): δ 3.51–3.55(1H, m, C-4′H_α), 3.62–3.71 (3H, m, C-2′H, C-3′H and C-4′H_β), 4.35 (1H, t, J = 5.7 Hz, OH), 4.60 (1H, d, J = 6.8 Hz, OH), 4.67 (1H, d, J = 4.7 Hz, OH), 5.15 (1H, d, J = 4.7 Hz, OH), 5.25 (1H, d, J = 6.9 Hz, C-1′H), 7.33–7.38 (1H, m, C-4″H), 7.48–7.54 (2H, m, C-2″H and C-6″H), 7.93 (1H, s, C-5H) and 7.99 (2H, m, C-3″H and C-5″H); ^{13}C NMR (75.5 MHz, DMSO-d_6): δ 61.75, 63.87, 69.29 and 72.18 (C-1′, C-2′, C-3′ and C-4′), 116.27 (C-3″ and C-5″), 125.23 (C-4″), 127.55 (C-2″ and C-6″), 133.26 (C-5), 137.67 (C-1″) and 151.06 (C-4); EIMS, *m*/*z* (% rel. int.): 247([M-18]$^+$, 10), 187 (15), 174 (100), 159 (5), 91 (45) and 77 (32).

2-Phenyl-4-(D-*arabino*-di-*O*-1′,2′,3′,4′-*iso*propylidenebutyl)-2H-1,2,3-triazole (2). A suspension of tetrahydroxybutyltriazole (1, 1.3 g, 5 mmol) and anhydrous $FeCl_3$ (750 mg) in dry acetone (125 mL) was stirred at 25–28 °C and the progress of the reaction was monitored by TLC. On completion, the reaction was terminated by addition of 10% solution of potassium carbonate (10 mL); solvent removed under reduced pressure and the brown syrup obtained was extracted with chloroform (3×50 mL). The combined organic layer was washed with water (2×50 mL), dried over Na_2SO_4 and solvent removed under reduced pressure to afford the crude product which was purified by silica gel column chromatography using petroleum ether–ethyl acetate as eluent to obtain pure di-*O*-*iso*propylidene derivative **2** as a colourless viscous oil (1.6 g) in 90% yield. R_f 0.30 (petroleum ether–ethyl acetate, 9:1); IR (Nujol): 1600, 1499, 1463, 1372, 1217, 1071, 967, 844

and 755 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.18, 1.22, 1.40 and 1.42 (12H, 4s, 3H each, 4×CH_3), 3.94 and 4.04 (2H, 2dd, 1H each, $J=4.7$ Hz and 8.6 Hz, and 6.1 Hz and 8.6 Hz, respectively, C-4′H_α and C-4′ H_β), 4.15–4.21 (1H, m, C-3′H), 4.27 (1H, t, $J=7.1$ Hz, C-2′H), 5.09 (1H, d, $J=7.2$ Hz, C-1′H), 7.20–7.29 (1H, m, C-4″H), 7.33–7.39 (2H, m, C-2″H and C-6″H), 7.73 (1H, s, C-5H) and 7.96–7.99 (2H, m, C-3″H and C-5″H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 24.19, 25.42, 25.79 and 26.05 (4×CH_3), 65.85 (C-4′), 72.80 and 76.50 (C-2′ and C-3′), 80.23 (C-1′), 108.74 and 109.58 (2×$C(CH_3)_2$), 117.84 (C-3″ and C-5″), 126.48 (C-4″), 128.19 (C-2″ and C-6″), 133.36 (C-5), 138.77 (C-1″) and 147.21 (C-4); EIMS, *m*/*z* (% rel. int.): 345 ([M^+], 25), 330 (25), 272 (30), 229 (100), 188 (95), 158 (50), 101 (95), 91 (25), 77 (40) and 43 (95).

2-Phenyl-4-(D-*arabino*-*O*-1′,2′-*iso*propylidene-3′,4′-dihydroxybutyl)-2H-1,2,3-triazole (3). A solution of **2** (1.4 g, 4 mmol) in 80% acetic acid (50 mL) was stirred at 25–28 °C for 12 h when TLC showed complete conversion of starting material into a slow moving product. Removal of acetic acid under reduced pressure afforded the title compound **3** as a white solid (830 mg) in 68% yield; mp 65–66 °C. R_f 0.25 (petroleum ether–ethyl acetate, 7:3); IR (Nujol): 3420 (OH), 1599, 1498, 1462, 1375, 1242, 1216, 1070, 968, 889 and 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.47 and 1.54 (6H, 2s, 3H each, 2×CH_3), 2.80 (2H, br s, 2×OH), 3.76–3.81 (2H, m, C-4′H), 4.04–4.08 (1H, m, C-3′H), 4.30–4.34 (1H, m, C-2′H), 5.25 (1H, d, $J=7.7$ Hz, C-1′H), 7.33–7.38 (1H, m, C-4″H), 7.45–7.49 (2H, m, C-2″H and C-6″H), 7.85 (1H, s, C-5H) and 7.98–8.01 (2H, m, C-3″H and C-5″H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 26.38 and 26.75 (2×CH_3), 63.12 (C-4′), 71.39 and 72.17 (C-2′ and C-3′), 81.32 (C-1′), 110.00 ($C(CH_3)_2$), 118.75(C-3″ and C-5″), 127.72 and 129.27 (C-2″, C-4″ and C-6″), 133.85 (C-5), 140.00 (C-1″) and 150.00 (C-4); EIMS, *m*/*z* (% rel. int.): 304 ([M-1]$^+$, 20), 289 (30), 230 (35), 216 (75), 188 (100), 158 (55), 91 (40), 77 (60) and 43 (95).

2-Phenyl-4-(D-*threo*-*O*-1,2-*iso*propylidene-3′-hydroxypropyl)-2H-1,2,3-triazole (4). To a solution of **3** (762 mg, 2.5 mmol) in 1:1 mixture of H_2O–dioxane (25 mL), $NaIO_4$ (2.5 mmol, 532 mg in 8 mL water) was added and the reaction mixture was stirred for 90 min at 25–28 °C when TLC showed complete conversion of the starting material into a fast moving product. Ethanol (15 mL) was added to the reaction mixture, the white solid that precipitated out was filtered off, $NaBH_4$ (47 mg, 1.25 mmol) was added to the clear filtrate and the contents stirred for 30 min at 25–28 °C. The reaction mixture was filtered, solvent evaporated under reduced pressure and the crude product thus obtained was purified by column chromatography on silica gel using petroleum ether–ethyl acetate (9:1) as eluent to afford *iso*propylidenepropyltriazole **4** as a colourless oil (605 mg) in 88% yield. R_f 0.45 (petroleum ether–ethyl acetate, 3:2); IR (Nujol): 3447 (OH), 1599, 1462, 1375, 1220, 1164, 1070, 968, 857 and 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 1.54 and 1.55 (6H, 2s, 3H each, 2×CH_3), 2.25 (1H, br s, OH), 3.79–3.83 and 4.10–4.13 (2H, 2m, 1H each, C-3′H_α and C-3′ H_β), 4.27–4.30 (1H, m, C-2′H), 5.17 (1H, d, $J=8.4$ Hz, C-1′H), 7.33–7.38 (1H, m, C-4″H), 7.45–7.50 (2H, m, C-2″H and C-6″H), 7.84 (1H, s, C-5H) and 8.03–8.06 (2H, m, C-3″H and C-5″H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 27.15 and 27.33 (2×CH_3), 61.37 (C-3′), 72.17 (C-2′), 81.99 (C-1′), 110.63 ($C(CH_3)_2$), 119.26 (C-4″), 128.02 (C-3″ and C-5″), 129.63 (C-2″ and C-6″), 134.27 (C-5), 140.04 (C-1″) and 148.04 (C-4); EIMS, *m*/*z* (% rel. int.): 275([M]$^+$, 36), 260 (75), 242 (15), 230 (10), 218 (95), 216 (5), 200 (75), 188 (75), 131 (15), 91 (65), 77 (95) and 59 (100).

2-Phenyl-4-(D-*threo*-1′,2′,3′-trihydroxypropyl)-2H-1,2,3-triazole (5). A solution of the *iso*propylidenetriazole **4** (550 mg, 2 mmol) in 80% acetic acid (25 mL) was refluxed for 2 h when TLC showed complete conversion of the starting material into a slow moving spot. The solvent was evaporated under reduced pressure to afford the trihydroxypropyltriazole **5** as a white crystalline solid (282 mg) in 60% yield; mp 87–89 °C (lit[21] mp 88–90 °C). R_f 0.35 (chloroform–methanol, 9:1); IR (Nujol): 3292 (OH), 1597, 1501, 1448, 1379, 1265, 1087, 942, 892 and 753 cm^{-1}; ^1H NMR (300 MHz, CD_3OD): δ 3.60 (1H, dd, $J=6.3$ Hz and 11.2 Hz, C-3′H_α), 3.74 (1H, dd, $J=5.2$ Hz and 11.2 Hz, C-3′ H_β), 3.92–3.97 (1H, q, $J=5.1$ Hz, C-2′H), 4.99 (1H, d, $J=4.8$ Hz, C-1′H), 7.35–7.40 (1H, m, C-4″H), 7.49–7.54 (2H, m, C-2″H and C-6″H), 7.93 (1H, s, C-5H) and 8.04–8.07 (2H, m, C-3″H and C-5″H); ^{13}C NMR (75.5 MHz, CD_3OD): δ 60.98 and 64.95 (C-2′ and C-3′), 72.25 (C-1′), 116.36 (C-4″), 125.10 (C-3″ and C-5″), 127.13 (C-2″ and C-6″), 132.46 (C-5), 137.60 (C-1″) and 149.32 (C-4); EIMS, *m*/*z* (% rel. int.): 235 ([M]$^+$, 10), 218 (15), 189 (10), 174 (100), 149 (25), 91 (55), 83 (85) and 77 (45).

General procedure of *Candida antarctica* lipase-catalysed acetylation of triazolyl sugars 1, 3 and 5

To a solution of the triazolyl sugar (**1**, **3** or **5**, 1 mmol) in dry diisopropyl ether (20 mL) was added vinyl acetate (4.4 mmol), followed by *C. antarctica* lipase (150 mg). The suspension was stirred at 42–45 °C in an incubator shaker and progress of the reaction monitored periodically by HPLC and/or TLC. The reaction was quenched on completion by filtering off the enzyme and the solvent evaporated to dryness in vacuo to afford the pure partially acetylated triazolyl sugars **6**–**8** in 95–98% yields.

2-Phenyl-4-(D-*arabino*-4′-acetoxy-1′,2′,3′-trihydroxybutyl)-2H-1,2,3-triazole (6). It was obtained as a white solid (301 mg) in 98% yield; mp 112–13 °C. R_f 0.40 (petroleum ether–ethyl acetate, 9:1); IR (Nujol): 3316 (OH), 1738 (O*C*OCH_3), 1598, 1461, 1377, 1071, 967 and 754 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 2.12 (3H, s, OCOCH_3), 3.07, 3.17 and 3.38 (3H, 3br s, 1H each, 3×OH), 3.97–4.10 (2H, m, C-4′H), 4.31–4.37 and 4.42–4.48 (2H, 2m, 1H each, C-2′H and C-3′H), 5.26 (1H, br s, C-1′H), 7.32–7.37 (1H, m, C-4″H), 7.45–7.49 (2H, m, C-2″H and C-6″H), 7.88 (1H, s, C-5H) and 7.99–8.02 (2H, m, C-3″H and C-5″H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.28 (OCO*C*H_3), 66.70 (C-4′), 70.98 and 73.36 (C-2′ and C-3′), 77.83 (C-1′), 119.25 (C-3″ and C-5″), 128.10 and 129.72 (C-2″, C-4″ and C-6″), 134.72 (C-5), 139.97

(C-1″), 150.46 (C-4) and 172.36 (CO); EIMS, *m*/*z* (% rel. int.): 247 ([M–CH_2CO–H_2O]$^+$, 8), 172 (100), 158 (15), 117 (12), 91 (88), 77 (58), 64 (31) and 43 (74).

2-Phenyl-4-(D-*arabino*-4′-acetoxy-*O*-1′,2′-*iso*propylidene-3′-hydroxybutyl)-2H-1,2,3-triazole (7). It was obtained as a colourless viscous oil (330 mg) in 95% yield. R_f 0.35 (petroleum ether–ethyl acetate, 9:1); IR (Nujol): 3446 (OH), 1741 (O*CO*CH_3), 1462, 1376, 1241, 1071, 967 and 758 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.51 and 1.53 (6H, 2s, 3H each, 2×CH_3), 2.04 (3H, s, OCOCH_3), 2.85 (1H, br s, OH), 4.16–4.21 (2H, m, C-4′H), 4.29–4.36 (2H, m, C-2′H and C-3′H), 5.28 (1H, d, J = 7.6 Hz, C-1′H), 7.33–7.36 (1H, m, C-4″H), 7.45–7.51 (2H, m, C-2″H and C-6″H), 7.84 (1H, s, C-5H) and 8.02–8.05 (2H, m, C-3″H and C-5″H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 26.58 and 26.83 (2×CH_3), 29.61 (OCO*C*H_3), 61.97 and 65.44 (C-3′ and C-4′), 70.35 (C-2′), 80.57 (C-1′), 110.41 (*C*(CH_3)$_2$), 118.81 (C-3″ and C-5″), 127.64 and 129.22 (C-2″, C-4″ and C-6″), 133.92 (C-5), 139.52 (C-1″), 148.22 (C-4) and 171.11 (CO); EIMS, *m*/*z* (% rel. int.): 347 ([M]$^+$, 45), 332 (35), 290 (50), 272 (25), 230 (60), 188 (100), 158 (60), 135 (10), 103 (30), 91 (40) and 77 (60).

2-Phenyl-4-(D-*threo*-3′-acetoxy-1′,2′-dihydroxypropyl)-2H-1,2,3-triazole (8). It was obtained as a white solid (269 mg) in 97% yield; mp 131–32 °C. R_f 0.50 (petroleum ether–ethyl acetate, 9:1); IR (Nujol): 3357 (OH), 1736 (O*CO*CH_3), 1461, 1376, 1228, 1062, 977, 810 and 757 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.10 (3H, s, OCOCH_3), 3.09 and 3.16 (2H, 2br s, 1H each, 2×OH), 4.20–4.27 and 4.29–4.37 (3H, 2m, 2H and 1H each, respectively, C-2′H and C-3′H), 4.95(1H, br s, C-1′H), 7.33–7.38 (1H, m, C-4″H), 7.45–7.50 (2H, m, C-2″H and C-6″H), 7.86 (1H, s, C-5H) and 8.01–8.04 (2H, m, C-3″H and C-5″H); ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 21.23 (OCO*C*H_3), 65.44 and 67.48 (C-2′ and C-3′), 72.54 (C-1′), 119.26 (C-3″ and C-5″), 128.13 and 129.72 (C-2″, C-4″ and C-6″), 134.52 (C-5), 139.99 (C-1″), 149.65 (C-4) and 171.74 (CO); EIMS, *m*/*z* (% rel. int.): 277 ([M]$^+$, 10), 260 (15), 234 (7), 217 (15), 200 (10), 174 (100), 91 (45) and 77 (40).

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References and Notes

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