

## Synthesis of Nonionic Surfactants. Sugar-Substituted Ether-Linked *Bis*-1,2,3-Triazoles†

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This work describes the synthesis of sugar-based ether-linked *bis*-1,2,3-triazoles. In the first approach, in which the heterocyclic portion was constructed from the click 1,3-dipolar cycloaddition of *n*-octyl azide and *n*-nonyl azide respectively with propargyl alcohol. Compounds **3** and **4** were readily prepared under phase transfer conditions from the corresponding triazolyl alcohols **1** and **2** and propargyl bromide. Two sugar azides starting from D-glucose and D-galactose were made to react with each of propargyl ethers **3** and **4** under Cu(I)-catalyzed Huisgen-Meldal 1,3-dipolar cycloaddition conditions. This reaction proceeded with excellent regioselectivity to afford the desired 1,4-disubstituted derivatives **5-8** in good yields. Bistriazoles **5** and **6** were deprotected under basic conditions. The effect of compounds **5-10** on the surface tension of water and some organic solvents like *m*-xylene will be measured in next subsequent study.

**Key Words:** Alkynyl triazoles, Click chemistry, *Bis*-1,2,3-triazoles, Surfactants, Sugars surfactants.

### INTRODUCTION

1,2,3-Triazoles are a significant category of heterocyclic compounds because of their wide range of utilities as synthetic intermediates and pharmaceuticals<sup>1</sup>. The chemistry of 1,2,3-triazoles was afterward developed in equivalent by Meldal *et al.*<sup>2</sup> and the group of Sharpless *et al.*<sup>2,3</sup> and known as 'click chemistry'. Two types of new *bis*-1,2,3-triazoles have been prepared from two essential sugars D-glucose and D-mannitol<sup>4</sup>. In previous years a great interest in work including the synthesis and study of surfactants based on naturally occurring compounds. Models are surfactants based on saccharides<sup>5-7</sup>, sterols<sup>8</sup> and fatty acids<sup>9</sup>. Such surfactants are interesting because they are generally easily biodegraded<sup>10</sup>. Carbohydrate-based surfactants have long been of interest due to their desirable performance properties and their potential to be derived from renewable feedstock. While most sugar based surfactants use an *O*-glycosidic bond, modern advances in carbohydrate C-C bond formation permits for the facile production of new types of sugar-based surfactants on a C-glycosidic bond<sup>11</sup>. 1-Nonyl-4-[(6-deoxy-1,2:3,4-Di-O-isopropylidene- $\alpha$ -D-galactos-6-yl)oxymethyl]-1*H*-1,2,3-triazole was prepared *via* click chemistry starting from D-galactose<sup>12</sup>. Ali *et al.*<sup>13</sup> prepared high yield water soluble 1,2,3-triazole starting from D-mannose using Cu(I) as a catalyst. Mixtures of sugar-based decanoyl-*N*-methylglucamide with different *n*-alkyltrimethyl ammonium bromides have been

studied using conductance and fluorescence spectroscopic techniques<sup>14</sup>. Francis *et al.*<sup>15</sup> synthesized a number of hydrophilic fluorosurfactants based on *bis*triazoles also sugar based fluorosurfactants were recently synthesized<sup>16</sup>. In this work novel sugar-substituted ether-linked *bis*-1,2,3-triazoles using click conditions were synthesized as a model of new nonionic surfactants.

### EXPERIMENTAL

Chemical were obtained from Ajax and Sigma-Aldrich Chemical. Infrared spectra were recorded using AVATAR 320 FT-IR. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using 300 MHz, Bruker DPX spectrometers, NMR assignments of the intended compounds supported by COSY and HSQC. Microelemental analysis was performed with elemental analyzer EA-300 eurovector. Silica TLC plates were used with an aluminum backing (0.2 mm, 60 F<sub>254</sub>). The reactions were monitored by TLC and visualized by development of the TLC plates with an alkaline potassium permanganate dip.

**Synthesis of triazolyl alcohols:** Triazolyl alcohols **1** and **2** were synthesized according to the previous work<sup>15</sup> starting from corresponding alkyl azides.

**Synthesis of alkynyl triazoles:** Triazolyl alcohol (1.7 mmol) was dissolved in DMF (10 mL) and NaOH pellets (0.25 g, 6.3 mmol) were added. The mixture was cooled to -20 °C stirred vigorously for 10 min in an ice bath under N<sub>2</sub>, then propargyl bromide (20 mL of 80 % solution in toluene, 0.214

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g, 1.8 mmol) was added dropwise and the heterogeneous reaction mixture was stirred vigorously for 24 h, slowly warming to room temperature. The mixture was filtered and H<sub>2</sub>O (30 mL) was added and the product was extracted with EtOAc (4 × 50 mL). The organic phases were combined and washed sequentially with 5 % HCl (2 × 30 mL) and H<sub>2</sub>O (30 mL). The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under reduced pressure. The resulting yellow liquid was flash chromatographed over silica gel (Et<sub>2</sub>O/hexane, 1:1) to generate alkynyl triazoles

**1-*n*-Octyl-4-((prop-2-ynyl)oxy)methyl)-1*H*-1,2,3-triazole (3):** Pale yellow oil (0.34 g, 80 %) (found: C, 67.45; H, 9.33; N, 16.84 % for C<sub>14</sub>H<sub>23</sub>N<sub>3</sub>O requires C, 67.43; H, 9.30; N, 16.85 %), IR (neat, cm<sup>-1</sup>): 3288, 3137, 2926, 2856, 2111, 1465, 1358, 1336, 1221, 1141, 1083, 1050, 1023. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.84 (t, *J* 6.4 Hz, 3H, CH<sub>3</sub>), 1.27 (m, 10H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.87 (m, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 2.45 (t, *J* 2.4 Hz, 1H, OCH<sub>2</sub>CCH), 4.20 (d, *J* 2.4 Hz, 2H, OCH<sub>2</sub>CCH), 4.32 (t, *J* 7.2 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.71 (s, 2H, 4-CH<sub>2</sub>O), 7.54 (s, 1H, H5). <sup>13</sup>C NMR (75 MHz) δ: 14.0 (CH<sub>3</sub>), 22.5 (CH<sub>2</sub>CH<sub>3</sub>), 26.4 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 31.6 (N1CH<sub>2</sub>CH<sub>2</sub>), 50.4 (N1CH<sub>2</sub>CH<sub>2</sub>), 57.4 (4-CH<sub>2</sub>O), 63.0 (OCH<sub>2</sub>CCH), 74.9 (OCH<sub>2</sub>CCH), 79.3 (OCH<sub>2</sub>CCH), 122.6 (C5-H), 144.2 (C4).

**1-*n*-Nonyl-4-((prop-2-ynyl)oxy)methyl)-1*H*-1,2,3-triazole (4):** White needles (0.36 g, 81 %) (found: C, 68.38; H, 9.58; N, 15.91 % for C<sub>15</sub>H<sub>25</sub>N<sub>3</sub>O requires C, 68.40; H, 9.57; N, 15.95%), m.p. 77-79 °C. IR (neat, cm<sup>-1</sup>): 3289, 3136, 2926, 2856, 2114, 1464, 1358, 1336, 1262, 1221, 1141, 1082, 1050, 1023, 941, 890, 818, 783. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.86 (t, *J* 6.9 Hz, 3H, CH<sub>2</sub>CH<sub>3</sub>), 1.24 (m, 8H, (CH<sub>2</sub>)<sub>4</sub>), 1.30 (m, 4H, (CH<sub>2</sub>)<sub>2</sub>), 1.89 (tt, *J* 7.2, 7.0 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 2.46 (t, *J* 2.4 Hz, 1H, OCH<sub>2</sub>CCH), 4.22 (d, *J* 2.4 Hz, 2H, OCH<sub>2</sub>CCH), 4.34 (t, *J* 7.2 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.74 (d, *J* 0.5 Hz, 2H, 4-CH<sub>2</sub>O), 7.56 (s, 1H, H5). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 14.0 (CH<sub>3</sub>), 22.6 (CH<sub>2</sub>CH<sub>3</sub>), 26.4 (CH<sub>2</sub>), 28.9 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 31.7 (N1CH<sub>2</sub>CH<sub>2</sub>), 50.5 (N1CH<sub>2</sub>CH<sub>2</sub>), 57.5 (4-CH<sub>2</sub>O), 62.9 (OCH<sub>2</sub>CCH), 74.9 (OCH<sub>2</sub>CCH), 79.2 (OCH<sub>2</sub>CCH), 122.6 (C5-H), 144.1 (C4).

**Synthesis of bis-triazoles:** Alkynyl triazole (1.0 mmol) and 2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl azide or 6-azido-6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactose (1.0 mmol) were added to a suspension of sodium ascorbate (0.018 g, 0.09 mmol) and CuSO<sub>4</sub>·5H<sub>2</sub>O (0.011 g, 0.045 mmol) in DMSO (5 mL). The mixture was heated to 70 °C and stirred for 48 h. The reaction mixture was diluted with water (30 mL), extracted with EtOAc (3 × 30 mL) and the combined organic layers washed with brine (2 × 20 mL), dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness under reduced pressure. The residue was flash chromatographed (silica gel, EtOAc/*n*-hexane 1:1) to yield the desired compounds.

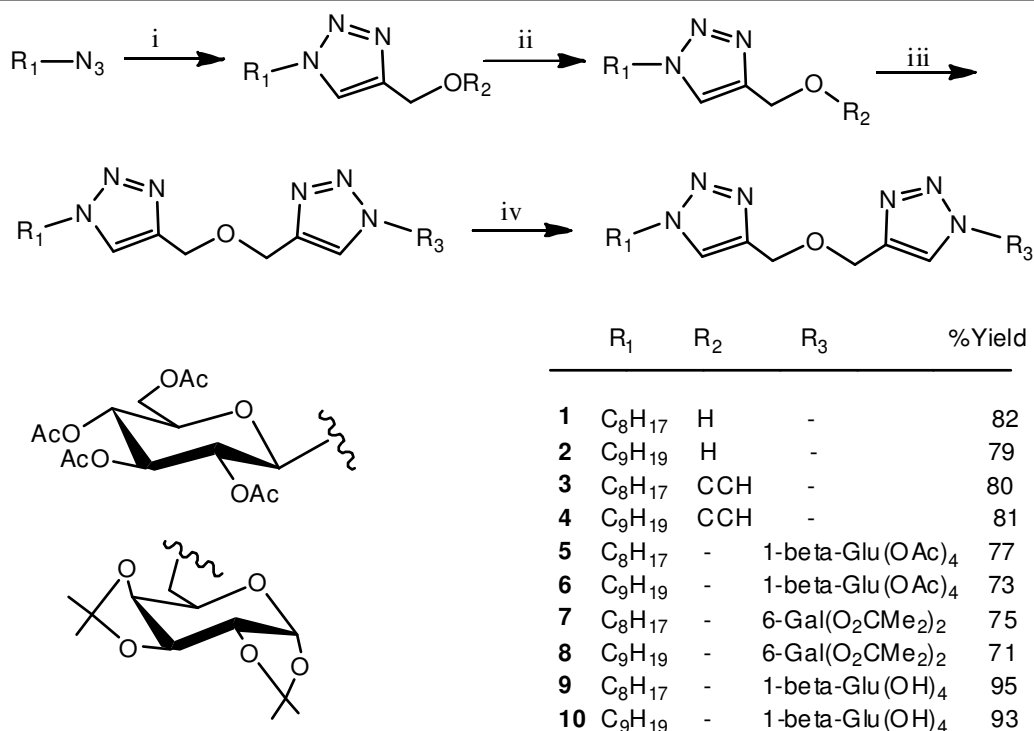
**4-[[1-*n*-Octyl-1*H*-1,2,3-triazol-4-yl)methoxy]methyl]-1-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-1*H*-1,2,3-triazole (5):** White solid (0.48 g, 77 %) (Found: C, 53.99; H, 6.83; N, 13.51 % for C<sub>28</sub>H<sub>42</sub>N<sub>6</sub>O<sub>10</sub> requires C, 54.01; H, 6.80; N, 13.50 %), m.p. 158-160 °C, R<sub>f</sub> = 0.22 (EtOAc/*n*-hexane 2:1). [α]<sub>D</sub><sup>20</sup> = +77.3 (c 1.0, CHCl<sub>3</sub>). IR (Nujol, cm<sup>-1</sup>): 3079, 2922, 2853, 1746, 1456, 1374, 1255, 1222, 1093, 1046. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.85 (t, *J* 6.3 Hz, 3H, CH<sub>3</sub>), 1.30 (m, 10H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.86 (m, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 2.01, 2.05, 2.07

(s, 12H, CH<sub>3</sub> acetate), 3.99 (m, 1H, H5<sup>''</sup>), 4.15 (dd, *J* 12.5, 1.9 Hz, 1H, Ha6<sup>''</sup>), 4.27 (dd, *J* 12.5, 4.8 Hz, 1H, Hb6<sup>''</sup>), 4.33 (t, *J* 7.2 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.69, 4.70 (s, 4H, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 5.22 (m, 1H, H4<sup>''</sup>), 5.44 (m, 2H, H3<sup>''</sup> and H2<sup>''</sup>), 5.88 (m, 1H, H1<sup>''</sup>), 7.57 and 7.82 (s, 2H, H5 and H5<sup>''</sup>). <sup>13</sup>C NMR (75 MHz) δ: 14.2 (CH<sub>3</sub>), 20.3, 20.6, 20.7, 20.8 (4C, CH<sub>3</sub> acetate), 22.7 (CH<sub>2</sub>CH<sub>3</sub>), 26.4 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 29.13 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 31.8 (N1CH<sub>2</sub>CH<sub>2</sub>), 50.5 (N1CH<sub>2</sub>CH<sub>2</sub>), 61.4 (C6<sup>''</sup>), 63.5, 63.8 (2C, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 67.8 (C4<sup>''</sup>), 70.5, 72.8 (2C, C3<sup>''</sup>, C2<sup>''</sup>), 75.2 (C5<sup>''</sup>), 85.9 (C1<sup>''</sup>), 121.4, 122.7 (2C, C5-H, C5'-H) 144.6, 145.6 (2C, C4, C4'), 169.0, 169.5, 170.0, 170.6 (4C, C=O).

**4-[[1-*n*-Nonyl-1*H*-1,2,3-triazol-4-yl)methoxy]methyl]-1-(2,3,4,6-tetra-*O*-acetyl-β-*D*-glucopyranosyl)-1*H*-1,2,3-triazole (6):** White solid (0.46 g, 73 %) (found: C, 54.72; H, 7.00; N, 13.23 % for C<sub>29</sub>H<sub>44</sub>N<sub>6</sub>O<sub>10</sub> requires C, 54.71; H, 6.97; N, 13.20 %), m.p. 167-169 °C, R<sub>f</sub> = 0.21 (EtOAc/*n*-hexane 2:1). [α]<sub>D</sub><sup>20</sup> = +38.2 (c 1.0, CHCl<sub>3</sub>). IR (Nujol, cm<sup>-1</sup>): 3076, 2957, 2922, 2852, 1744, 1453, 1372, 1256, 1220, 1094, 1046. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.86 (t, *J* 6.3 Hz, 3H, CH<sub>3</sub>), 1.28 (m, 12H, (CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 1.89 (m, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 1.87, 2.02, 2.06, 2.07 (s, 12H, CH<sub>3</sub> acetate), 3.99 (m, 1H, H5<sup>''</sup>), 4.15 (dd, *J* 12.5, 1.9 Hz, 1H, Ha6<sup>''</sup>), 4.28 (dd, *J* 12.5, 4.8 Hz, 1H, Hb6<sup>''</sup>), 4.32 (t, *J* 7.4 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.71 (s, 4H, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 5.22 (m, 1H, H4<sup>''</sup>), 5.42 (m, 2H, H3<sup>''</sup> and H2<sup>''</sup>), 5.87 (m, 1H, H1<sup>''</sup>), 7.61 and 7.85 (s, 2H, H5 and H5<sup>''</sup>). <sup>13</sup>C NMR (75 MHz) δ: 14.2 (CH<sub>3</sub>), 20.3, 20.6, 20.7, 20.8 (4C, CH<sub>3</sub> acetate), 22.7 (CH<sub>2</sub>CH<sub>3</sub>), 26.6 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 31.9 (N1CH<sub>2</sub>CH<sub>2</sub>), 50.8 (N1CH<sub>2</sub>CH<sub>2</sub>), 61.6 (C6<sup>''</sup>), 63.5, 63.9 (2C, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 67.8 (C4<sup>''</sup>), 70.5, 72.9 (2C, C3<sup>''</sup>, C2<sup>''</sup>), 75.2 (C5<sup>''</sup>), 85.7 (C1<sup>''</sup>), 121.5, 123.0 (2C, C5-H, C5'-H) 144.5, 145.4 (2C, C4, C4'), 169.1, 169.5, 170.0, 170.6 (4C, C=O).

**4-[[1-*n*-Octyl-1*H*-1,2,3-triazol-4-yl)methoxy]methyl]-1-(6-Deoxy-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactose-6-yl)-1*H*-1,2,3-triazole (7):** White solid (0.40 g, 75 %) (found: C, 58.44; H, 7.95; N, 15.70 % for C<sub>26</sub>H<sub>42</sub>N<sub>6</sub>O<sub>6</sub> requires C, C, 58.41; H, 7.92; N, 15.72 %), m.p. 133-135 °C, R<sub>f</sub> = 0.26 (EtOAc/*n*-hexane 2:1). [α]<sub>D</sub><sup>20</sup> = +55.9 (c 1.0, CHCl<sub>3</sub>). IR (Nujol, cm<sup>-1</sup>): 3095, 3062, 2950, 2922, 2853, 1468, 1374, 1239, 1221, 1165, 1097, 1006, 991, 920, 856. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.86 (t, *J* 6.2 Hz, 3H, CH<sub>3</sub>), 1.27 (m, 10H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.31, 1.35, 1.38, 1.48 (s, 12H, CH<sub>3</sub> isopropylidene), 1.88 (m, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.17, 4.19 (2H, H4<sup>''</sup>, H5<sup>''</sup>), 4.31 (dd, *J* 7.5, 4.9 Hz, 1H, H2<sup>''</sup>), 4.33 (t, *J* 7.1 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.45 (dd, *J* 14.4, 8.3 Hz, 1H, Ha6<sup>''</sup>), 4.62 (dd, *J* 7.5, 5.0 Hz, 1H, Hb6<sup>''</sup>), 4.65 (dd, *J* 7.8, 2.4 Hz, 1H, H3<sup>''</sup>) 4.68, 4.70 (s, 4H, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 5.51 (d, *J* 4.9 Hz 1H, H1<sup>''</sup>), 7.56 and 7.75 (s, 2H, H5 and H5<sup>''</sup>). <sup>13</sup>C NMR (75 MHz) δ: 14.2 (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>CH<sub>3</sub>), 24.6, 25.0, 26.0, 26.1 (4C, CH<sub>3</sub> isopropylidene), 26.6 (CH<sub>2</sub>), 29.0 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 31.8 (N1CH<sub>2</sub>CH<sub>2</sub>), 50.5 (C6<sup>''</sup>), 50.6 (N1CH<sub>2</sub>CH<sub>2</sub>), 63.6, 63.62 (2C, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 67.3 (C5<sup>''</sup>), 70.4 (C2<sup>''</sup>), 70.9 (C3<sup>''</sup>), 71.2 (C5<sup>''</sup>), 96.3 (C1<sup>''</sup>), 109.1 (1,2-*O*<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 110.0 (3,4-*O*<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 122.7, 124.4 (2C, C5-H, C5'-H) 144.4, 144.8.

**4-[[1-*n*-Nonyl-1*H*-1,2,3-triazol-4-yl)methoxy]methyl]-1-(6-deoxy-1,2:3,4-di-*O*-isopropylidene-α-*D*-galactose-6-yl)-1*H*-1,2,3-triazole (8):** White solid (0.39 g, 71 %) (found: C, 59.13; H, 8.11; N, 15.30 % for C<sub>27</sub>H<sub>44</sub>N<sub>6</sub>O<sub>6</sub> requires C, C,



Reagents and Conditions: i. HCCCH<sub>2</sub>OH, Na ascorbate, CuSO<sub>4</sub>·H<sub>2</sub>O, DMSO, 60°C, 36h; ii. HCCCH<sub>2</sub>Br, NaOH, DMF, -20°C-rt, 24h; iii. glucosyl azide, Na ascorbate, CuSO<sub>4</sub>·H<sub>2</sub>O, DMSO, 70°C, 48h; iv. (a) NaOMe, MeOH, r.t. 3h; (b) Amberlite IR 120 (H<sup>+</sup>), 15-20 min.

#### Scheme-I

59.10; H, 8.08; N, 15.32 %), m.p. 147-149 °C, R<sub>f</sub> = 0.25 (EtOAc/*n*-hexane 2:1). [α]<sub>D</sub><sup>20</sup> = +17.2 (c 1.0, CHCl<sub>3</sub>). IR (Nujol, cm<sup>-1</sup>): 3062, 2923, 2853, 1466, 1375, 1222, 1167, 1096, 1049, 1007. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 0.86 (t, *J* 6.1 Hz, 3H, CH<sub>3</sub>), 1.28 (m, 12H, (CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 1.31, 1.35, 1.38, 1.49 (s, 12H, CH<sub>3</sub> isopropylidene), 1.88 (m, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.17, 4.20 (2H, H4<sup>''</sup>, H5<sup>''</sup>), 4.31 (dd, *J* 7.5, 4.9 Hz, 1H, H2<sup>''</sup>), 4.32 (t, *J* 7.2 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.45 (dd, *J* 14.4, 8.3 Hz, 1H, Ha6<sup>''</sup>), 4.62 (dd, *J* 7.5, 5.0 Hz, 1H, Hb6<sup>''</sup>), 4.65 (dd, *J* 7.8, 2.4 Hz, 1H, H3<sup>''</sup>), 4.69, 4.70 (s, 4H, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 5.51 (d, *J* 4.9 Hz, 1H, H1<sup>''</sup>), 7.56 and 7.75 (s, 2H, H5 and H5'). <sup>13</sup>C NMR (75 MHz) δ: 14.2 (CH<sub>3</sub>), 22.7 (CH<sub>2</sub>CH<sub>3</sub>), 24.6, 25.0, 26.0, 26.1 (4C, CH<sub>3</sub> isopropylidene), 26.6 (CH<sub>2</sub>), 29.1 (CH<sub>2</sub>), 29.3 (CH<sub>2</sub>), 29.4 (CH<sub>2</sub>), 30.4 (CH<sub>2</sub>), 31.9 (N1CH<sub>2</sub>CH<sub>2</sub>), 50.5 (C6<sup>''</sup>), 50.6 (N1CH<sub>2</sub>CH<sub>2</sub>), 63.6, 63.62 (2C, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 67.3 (C5<sup>''</sup>), 70.4 (C2<sup>''</sup>), 70.9 (C3<sup>''</sup>), 71.2 (C5<sup>''</sup>), 96.3 (C1<sup>''</sup>), 109.1 (1,2-O<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 110.0 (3,4-O<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>), 122.7, 124.4 (2C, C5-H, C5'-H) 144.4, 144.8.

**Deprotection of bis-triazoles 5 and 6:** Methanolic NaOMe (0.20 mL, 0.1 mmol, 0.5 M) was added to a solution of protected triazoles **5** and **6** (1.0 mmol) in anhyd. MeOH (5 mL). The mixture was stirred for 3 h at r.t. then Amberlite IR 120 (H<sup>+</sup>) resin (1.3 g) was added. The mixture was allowed to stir until the neutralization occurred (15-20 min), the resin was filtered off. The filtrate was concentrated *in vacuo* to yellow syrup then the residue dissolved in small amount of EtOH and triturated with light pet. to afford the deprotected triazoles as a white solid.

**4-[(1-*n*-Octyl-1*H*-1,2,3-triazol-4-yl)methoxy]methyl]-1-(β-*D*-glucopyranosyl)-1*H*-1,2,3-triazole (**9**):** White solid

(0.43 g, 95 %), (found: C, 52.84; H, 7.54; N, 18.47 % for C<sub>20</sub>H<sub>34</sub>N<sub>6</sub>O<sub>6</sub> requires C, 52.85; H, 7.54; N, 18.49 %), m.p. 221-223 °C, R<sub>f</sub> = 0.31 (DCM/MeOH 15:1). [α]<sub>D</sub><sup>20</sup> = +11.1 (c 1.0, MeOH). IR (Nujol, cm<sup>-1</sup>): 3346, 3138, 2924, 2855, 1460, 1368, 1229, 1094, 1048, 903, 830. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ: 0.89 (t, *J* 6.3 Hz, 3H, CH<sub>3</sub>), 1.28 (m, 10H, (CH<sub>2</sub>)<sub>5</sub>CH<sub>3</sub>), 1.89 (m, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 3.56, 3.58 (m, 3H, H5<sup>''</sup>, H4<sup>''</sup>, H3<sup>''</sup>), 3.73 (dd, *J* 12.0, 5.0 Hz, 1H, Ha6<sup>''</sup>), 3.86 (m, 1H, Hb6<sup>''</sup>), 3.90 (m, 1H, H2<sup>''</sup>), 4.39 (t, *J* 7.1 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.66, 4.68 (s, 4H, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 5.63 (d, *J* 9.2 Hz, 1H, H1<sup>''</sup>), 7.97 and 8.21 (s, 2H, H5 and H5'). <sup>13</sup>C NMR (75 MHz) δ: 14.4 (CH<sub>3</sub>), 23.6 (CH<sub>2</sub>CH<sub>3</sub>), 27.5 (CH<sub>2</sub>), 30.0 (CH<sub>2</sub>), 30.2 (CH<sub>2</sub>), 31.2 (CH<sub>2</sub>), 32.9 (N1CH<sub>2</sub>CH<sub>2</sub>), 51.4 (N1CH<sub>2</sub>CH<sub>2</sub>), 62.4 (C6<sup>''</sup>), 64.0, 64.1 (2C, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 70.9 (C4<sup>''</sup>), 74.3 (C2<sup>''</sup>), 78.4 (C3<sup>''</sup>), 81.1 (C5<sup>''</sup>), 89.6 (C1<sup>''</sup>), 124.5, 125.1 (2C, C5-H, C5'-H) 145.6, 145.7 (2C, C4, C4').

**4-[(1-*n*-Nonyl-1*H*-1,2,3-triazol-4-yl)methoxy]methyl]-1-(β-*D*-glucopyranosyl)-1*H*-1,2,3-triazole (**10**):** White solid (0.44 g, 93 %), (Found: C, 53.81; H, 7.72; N, 17.93 % for C<sub>21</sub>H<sub>36</sub>N<sub>6</sub>O<sub>6</sub> requires C, 53.83; H, 7.74; N, 17.94 %), m.p. 233-235 °C, R<sub>f</sub> = 0.29 (DCM/MeOH 15:1). [α]<sub>D</sub><sup>20</sup> = +6.8 (c 1.0, MeOH). IR (Nujol, cm<sup>-1</sup>): 3345, 3138, 2923, 2855, 1460, 1368, 1229, 1093, 1048, 903, 831. <sup>1</sup>H NMR (300 MHz, CD<sub>3</sub>OD) δ: 0.89 (t, *J* 6.2 Hz, 3H, CH<sub>3</sub>), 1.28 (m, 12H, (CH<sub>2</sub>)<sub>6</sub>CH<sub>3</sub>), 1.89 (m, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 3.56, 3.58 (m, 3H, H5<sup>''</sup>, H4<sup>''</sup>, H3<sup>''</sup>), 3.73 (dd, *J* 12.0, 5.0 Hz, 1H, Ha6<sup>''</sup>), 3.86 (m, 1H, Hb6<sup>''</sup>), 3.90 (m, 1H, H2<sup>''</sup>), 4.39 (t, *J* 7.1 Hz, 2H, N1CH<sub>2</sub>CH<sub>2</sub>), 4.66, 4.68 (s, 4H, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 5.63 (d, *J* 9.1 Hz, 1H, H1<sup>''</sup>), 7.97 and 8.22 (s, 2H, H5 and H5'). <sup>13</sup>C NMR (75 MHz) δ: 14.4 (CH<sub>3</sub>), 23.7 (CH<sub>2</sub>CH<sub>3</sub>), 27.4 (CH<sub>2</sub>), 30.1 (CH<sub>2</sub>), 30.3

(CH<sub>2</sub>), 30.5 (CH<sub>2</sub>), 31.3 (CH<sub>2</sub>), 32.9 (N1CH<sub>2</sub>CH<sub>2</sub>), 51.4 (N1CH<sub>2</sub>CH<sub>2</sub>), 62.4 (C6''), 64.0, 64.03 (2C, 4-CH<sub>2</sub>O, 4'-CH<sub>2</sub>O), 70.9 (C4''), 74.0 (C2''), 78.4 (C3''), 81.1 (C5''), 89.6 (C1''), 124.5, 125.1 (2C, C5-H, C5'-H) 145.5, 145.6 (2C, C4, C4').

## RESULTS AND DISCUSSION

Regarding the amphiphilic structure of a typical surfactant with a hydrophilic head group and a hydrophobic tail, it has always been a challenge to attach a carbohydrate molecule as substitute to polyol such polyethylene glycol to a long chain substituent, such as a fatty acid or a fatty alcohol. It was decided to examine D-glucose and D-galactose substituted triazole derivatives because these sugars were very closely related in structure to each other, but also they allowed easy access to radically different points of attachment on the sugar and different forms of hydroxyl group protection to be tested. Fortunately, all the necessary building blocks for this study have been reported previously, but the combination of reactants have not been described and all the target compounds are new.

Cu(I) catalyzed cycloaddition reaction of *n*-octyl azide and *n*-nonyl azide with propargyl alcohol afforded the triazolyl alcohols **1** and **2** respectively in average very good yield (**Scheme-1**). Alcohols **1** and **2** were etherified using NaOH and propargyl bromide; this method gave the alkynyl ether in very good yield without further dark colour which afforded when NaH was used.

Another click reaction has been used to achieve the targeted *bis*-1,2,3-triazoles in good yield. The designed compounds are analogues for fatty acid glycosides and pseudoglycosidem. The melting points of the synthesized compounds increased as the chain length increased by means one methylene group also the other obvious factor affected the melting point was the protecting groups; the triazoles with glucose peracetate building blocks were higher melting points than those with diacetonidegalactose moiety. Alkynyl triazoles **3** and **4** were obtained in a very good yields, IR bands at 3288, 3289 cm<sup>-1</sup> are belong to the (C≡C-H) stretching in addition to the bands at 2111, 2114 cm<sup>-1</sup> (C≡C) stretching another evidence was predicted from <sup>1</sup>H NMR spectra of the mentioned compounds the triplets at 2.45, 2.46 ppm for the acetylenic protons and the doublets at 4.20, 4.22 ppm of the methylene protons (OCH<sub>2</sub>CCH). Many excellent proofs were obtained from both FT-IR and NMR spectra for the formation of the bistriazoles **5**, **6**, **7** and **8**. In FT-IR the disappearance of (C≡C) and (C≡C-H) while in <sup>1</sup>H NMR the disappearance of acetylenic proton signal

and presence a new singlet in the region 7.75-7.85 ppm. The *bis*-1,2,3-triazoles **7** and **8** were deprotected in methanol under basic conditions followed by neutralization by Amberlite IR 120 (H+) resin gave the corresponding triazoles **9** and **10** in excellent yields, the removal of acetate groups did not affect the ether linkage between triazole rings because we still have two singlets, which belong to two methylene protons at 4.66 and 4.68 ppm. Melting points increased sharply but the deprotection did not interrupt the stereo configuration of the overall molecules because the optical rotation values still positive. Meanwhile we are examining the effect of the synthesized bistriazoles on the surface tension of different solvents.

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## REFERENCES

1. J. Muldoon, Y. Lin, S. Silverman, W. Lindstrom, A. Olson, H. Kolb, M. Finn, K.B. Sharpless, J.H. Elder and V.V. Fokin, *Angew. Chem. Int. Ed.*, **45**, 1435 (2006).
2. H.C. Kolb and K.B. Sharpless, *Drug Discovery Today*, **8**, 1128 (2003).
3. V. Rostovtsev, L. Green, V. Fokin and K.B. Sharpless, *Angew. Chem., Int. Ed.*, **41**, 2596 (2002).
4. A.I. Mohammed and AL-Mustansiriyah, *J. Sci.*, **22**, 51 (2011).
5. I. Rico-Latter and A. Lattes, *Colloid. Surf. A*, **37**, 123 (1997).
6. L. Retaillieu, A. Laplace, H. Fensterbank and C. Larpent, *J. Org. Chem.*, **63**, 608 (1998).
7. D. Balzer, *Langmuir*, **9**, 3375 (1993).
8. B.M. Folmer, M. Svensson, K. Holmberg and W. Brown, *J. Coll. Int. Sci.*, **213**, 112 (1999).
9. D.B. Sarney, H. Kapeller, G. Fregapane and E.N. Vulfson, *J. Am. Oil Chem. Soc.*, **71**, 711 (1994).
10. B.M. Folmer, K. Holmberg, E. Gottberg-Klingskog and K. Bergström, *J. Surf. Det.*, **4**, 175 (2001).
11. P.M. Foley, A. Phimpachanh, E.S. Beach, J.B. Zimmermana and P.T. Anastasa, *Green Chem.*, **13**, 321 (2011).
12. R. Jwad, *J. AL-Nahrain Univ.*, **14**, 44 (2011).
13. Y. Ali, A.I. Mohammed and R.S. Jwad, Proceedings of 3rd Scientific Conference of the College of Science, University of Baghdad, Iraq, pp.1370-1374 (2009).
14. J.M. Hierrezuelo, J. Aguiar and C. C. Ruiz, *Colloid. Surf. A*, **264**, 29 (1997).
15. D.V. Francis, D.H. Miles, A.I. Mohammed, R.W. Read and X. Wang, *J. Fluorine Chem.*, **132**, 898 (2011).
16. A.M. Ahmed, A.I. Mohammed and R.W. Read, *J. Fluorine Chem.*, (to be submitted).