194. Convenient Synthesis of 2-Azido-2-deoxy-aldoses by Diazo Transfer

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Dedicated to Prof. Dr. *Antonio Gómez-Sánchez* on the occasion of his 65th birthday.

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Diazo transfer from trifluoromethanesulfonyl azide (TfN_3) to 2-amino-2-deoxy-glycoses constitutes a high-yielding, simple procedure for the preparation of partially protected or unprotected 2-azido-2-deoxy-aldoses. Thus, the D-allosamine derivative **2** gave 93% of **3**, while diazo transfer to D-glucosamine, D-mannosamine, and D-galactosamine, followed by acetylation, yielded the azides **5**, **7**, and **9** in yields of 74–91, 65, and 70%, respectively.

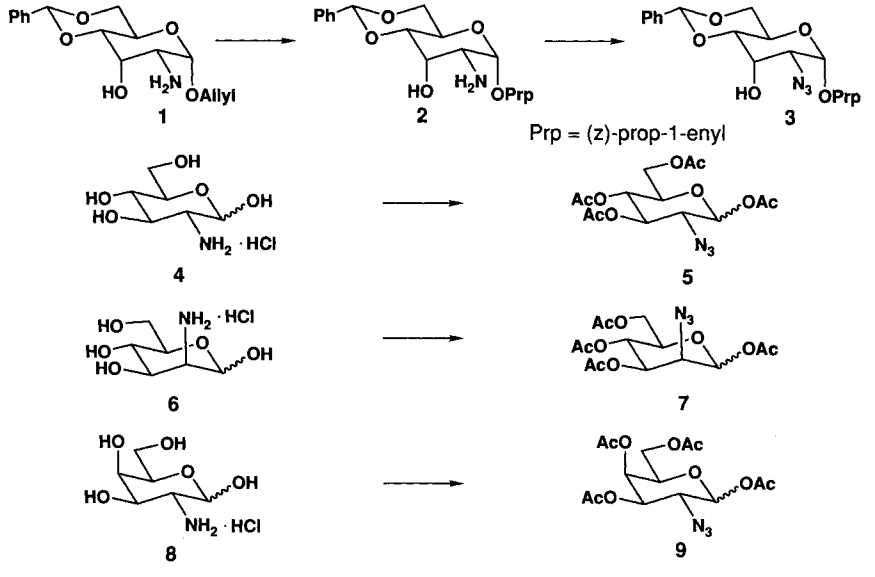
Introduction. – The 2-Azido-2-deoxy derivatives of mono- and disaccharides are frequently used intermediates in the synthesis of amino-deoxy oligosaccharides (see [1] for leading ref.). These azides have been prepared by azidonitration of glycals [2], by addition of halogeno azides to glycals [3], and from 1,6-anhydroglycoses either by opening of epoxides [4] or by substitution of 2-*O*-triflates [5]. The diastereoselectivity of the azidonitration and halogeno-azide addition depends on the configuration of the glycal. It is high for the *lyxo*-glycals, leading to mixtures of 2-azido-2-deoxy-galactose nitrates [2], and lower for the *arabino*-glycals, leading to mixtures of 2-azido-2-deoxy-glucose and -mannose derivatives [6]. The preparation of 2-azido-2-deoxy-glycals from 1,6-anhydro sugars proceeds in a configurationally controlled way, but requires a relatively large number of steps.

The 6-Azido-6-deoxyhexoses have also been prepared from the corresponding acetamides by *N*-nitrosation, reduction, and *N*-acylation to *N,N'*-diacylhydrazines, and again *N*-nitrosation [7]; this method has been modified [8] for the transformation of 1,3,4,6-tetra-*O*-acetyl-2-*N*-benzyl-2-deoxy-β-D-glucopyranose (prepared from glucosamine) into the corresponding azide β-D-**5** [3] (*cf. Scheme*) in 49–55% overall yield. Finally, the synthesis of 5-azido-3,5-dideoxy-D-*glycero*-D-*galacto*-nonulosonic acid [9] involved the reaction of HN_3 with a diazo compound which was prepared by *N*-nitrosation of a derivative of *N*-acetylneuraminic acid.

Glucosamine is a cheap starting material and available in large amounts. It can easily be transformed into derivatives of 2-amino-2-deoxy allose which was required for the synthesis of allosamidin [10]. A method allowing the direct transformation of 2-amino-2-deoxyaldoses, and particularly glucosamine, into the corresponding azides would be welcome in the context of the synthesis of oligosaccharides [1]. Amines can be transformed into azides by diazo transfer from trifluoromethanesulfonyl azide (TfN_3) but, to the best of our knowledge, this method has not been applied to carbohydrates[1]). To check the scope of the reaction, we examined the transformation of the partially protected derivative **2** of D-allosamine, of D-glucosamine (**4**), D-mannosamine (**6**), and D-galactosamine (**8**) into the corresponding azides.

Results. – The allosamine derivative **2** [10] was prepared from the allyl glycoside **1** [10] (see the *Scheme*). D-Glucosamine (**4**), D-mannosamine (**6**), and D-galactosamine (**8**) were liberated *in situ* from their commercially available hydrochlorides. Considering its hazardous nature, TfN_3 was prepared *in situ* [12] and used in solution only. The concentration of the TfN_3 solution was determined by IR spectroscopy (intensity of the band at 2150 cm^{-1}) to be 0.26M, using the easily available TsN_3 and a microanalytically pure sample of **3** as independent standards. The result compares well with the one obtained by titration of liberated TfOH [12]. For the transformation of the amines **4**, **6**, and **8**, the preparation of the TfN_3 soln. was slightly modified. Its concentration was 0.40M. The transformation of the allosamine derivative **2** proceeded smoothly in $MeCN/CH_2Cl_2$ at room temperature over 2 h to give the crystalline and stable azide **3** in high yield.

Scheme



[1]) *Araki et. al.* [11] have published the transformation of methyl 2-amino-4,6-*O*-benzylidene-2-deoxy-3-*O*-methyl-α-D-*altro*- and -α-D-*allo*-pyranoside into the corresponding azides in low yield using TsN_3/BuLi in benzene.

To overcome the problem of solubility of the amines **4**, **6**, and **8**, we chose a two-phase reaction in the presence of methyl(trioctyl)ammonium chloride as a phase-transfer agent, but the reaction was too slow to be of practical use. To ensure a homogeneous mixture, we added a solution of TfN_3 in CH_2Cl_2 to a solution of the amine in MeOH. In this manner, D-glucosamine (**4**) was transformed into the corresponding azide, which was isolated as a mixture of the anomeric acetates α- and β-D-**5** (74–91%). The synthesis of the *manno*- and *galacto*-azides **7** and **9**, respectively, proceeded similarly to the one of **5**, but yields were lower. Our procedure for the preparation of the 2-azido-2-deoxy derivatives **5**, **7**, and **9** of glucose, mannose, and galactose, respectively, compares favourably with the published ones.

The presence of a (*Z*)-propenyl substituent in **2** is evidenced in the ^{1}H-NMR spectrum by an apparent *quint.* at 4.66 ppm which is assigned to H–C(2'), the ^3J(1',2') value (6.2 Hz) being of the same magnitude as ^3J(2',Me). H–C(3) appears as a *t* with a small coupling constant of 2.6 Hz, as it is typical for a $^4C_1$ conformation. The broad signal at 1.89 ppm, which disappears upon addition of D_2O, is assigned to NH_2 and OH. In the ^{13}C-NMR spectrum of **2**, the signals at 142.14 (*d*), 104.60 (*d*), and 9.42 (*q*) are evidencing the (*Z*)-propenyl substituent. The IR spectrum of **3** shows an absorption at 3570 cm^{-1} which is assigned to the OH valence vibration. The absence of other absorptions above 3000 cm^{-1} and the band at 2110 cm^{-1} indicate the transformation of the amino into the azido function. This transformation has little effect on the conformation of the pyranose ring as evidenced by the coupling constants in the ^{1}H-NMR spectrum. The signal of the C(3)–OH group appears between 2.75 and 2.50 ppm as a br. *s*.

We thank Dr. *P. Dhar* for her help in checking the procedures.

Experimental Part

General. Solvents were distilled before use. Normal workup means drying the org. phase (Na_2SO_4), filtration through a cotton plug, and evaporation of the solvent *i.v.* Solns. were evaporated at or below 40° in a *Büchi* rotary evaporator. Samples were dried in high vacuum (h.v.) at a pressure below 0.1 mbar. Qual. TLC: *Merck* precoated silica gel *60 F-254* plates; detection by spraying the plates with a soln. of 0.02m I_2 and 0.30m KI in 10% aq. H_2SO_4 soln., followed by heating at *ca.* 200°. Flash chromatography (FC): silica gel *Merck 60* (40–63 μm). M.p.: uncorrected. Optical rotations: 1-dm cell; at 365, 436, 546, 578, and 589 nm; values at 589 nm were obtained from a regression curve. IR spectra: 3% soln. in $CHCl_3$. ^{1}H- and ^{13}C-NMR spectra: at 300 MHz (^{1}H) and at 50 MHz (^{13}C); chemical shifts δ in ppm relative to TMS and coupling constants *J* in Hz. MS: by EI at 70 eV and by CI (isobutane).

(Z)-Prop-1-enyl 2-Amino-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside (**2**). A soln. of **1** (3.97 g, 12.9 mmol) in DMSO (74 ml, dried over 4-Å molecular sieves) was added to a vigorously stirred suspension of *t*-BuOK (3.26 g, 29.1 mmol) in DMSO (74 ml). The slightly turbid brown mixture was heated to 50° under N_2 for 4 h 20 min, then poured onto 300 ml of ice-water, and extracted with Et_2O (4 × 250 ml). The org. phase was washed with H_2O and brine. Normal workup yielded 3.77 g (95%) of **2** as slightly yellow, crystalline material. An anal. sample was obtained by recrystallization in AcOEt/hexane. R_f (CH_2Cl_2/MeOH 95:5) 0.17. $[\alpha]_D^{25}$ = +58.3 (*c* = 1.1, $CHCl_3$). IR: 3550*w*, 3390*w*, 3320*w*, 2980*m*, 2940*m*, 2860*m*, 1670*s*, 1580*w*, 1450*w*, 1380*m*, 1340*m*, 1125*s*, 1100*s*, 1050*s*, 1000*s*, 960*s*, 910*m*, 880*m*. ^{1}H-NMR ($CDCl_3$): 7.55–7.50 (*m*, 2 arom. H); 7.42–7.33 (*m*, 3 arom. H); 6.10 (*qd*, *J* = 1.8, 6.2, 1 olef. H); 5.61 (*s*, PhC*H*); 4.99 (*d*, *J* = 3.9, H–C(1)); 4.66 (*quint.*, *J* = 6.7, 1 olef. H); 4.36 (*dd*, *J* = 5.2, 10.2, H_{eq}–C(6)); 4.15 (*t*, *J* = 2.6, H–C(3)); 4.13 (*dt*, *J* = 5.0, 10.0, H–C(5)); 3.75 (*t*, *J* = 10.3, H_{ax}–C(6)); 3.60 (*dd*, *J* = 2.8, 9.8, H–C(4)); 3.05 (*t*, *J* = 3.5, H–C(2)); 1.66 (*dd*, *J* = 1.7, 6.8, Me); 1.89 (br. *s*, exchanged by D_2O, NH_2, OH). ^{13}C-NMR ($CDCl_3$): 142.14 (*d*); 137.20 (*s*); 129.06 (*d*); 126.19 (*d*); 104.60 (*d*); 101.78 (*d*); 100.49 (*d*); 79.12; (*d*); 69.90 (*d*); 69.13 (*t*); 57.60 (*d*); 52.19 (*d*); 9.42 (*q*). CI-MS: 309 (11), 308 (56, [*M* + 1]$^+$), 251 (15), 250 (100). Anal. calc. for $C_{16}H_{21}NO_5$ (307.36): C 62.53, H 6.89, N 4.56; found: C 62.63, H 7.00, N 4.34.

(Z)-Prop-1-enyl 2-Azido-4,6-O-benzylidene-2-deoxy-α-D-allopyranoside (**3**). NaN_3 (8.00 g, 123.0 mmol) was dissolved at 23° in H_2O (20 ml) in a 50 ml flask, equipped with a septum and a N_2 balloon. CH_2Cl_2 (25 ml) was added to the vigorously stirred soln. at 0°. Tf_2O (freshly distilled over P_2O_5 under Ar; 4.1 ml, 25.0 mmol) was

added within 5 min by syringe. The mixture was stirred for 2 h at 0°, the org. layer was separated, and the aq. layer was extracted with CH_2Cl_2 (2 × 10 ml). The combined org. layers were extracted with sat. aq. $NaHCO_3$ soln. (20 ml) and H_2O (20 ml), dried (Na_2SO_4), filtered, and the TfN_3 soln. was stored at 4° over 4-Å molecular sieves, c = 0.26M.

To a soln. of **2** (2.50 g, 8.10 mmol) and 4-(dimethylamino)pyridine (4.35 g, 35.6 mmol; recrystallized in toluene) in MeCN (50 ml, distilled from CaH_2), TfN_3 soln. (39 ml, 10.9 mmol, as prepared above) was added at 23° within 10 min by syringe. After 2 h, the mixture was concentrated at 30° to *ca.* 3 ml. FC (125 g of SiO_2, CH_2Cl_2/MeOH 99:1) gave 2.42 g (93%) of **3**. R_f (hexane/AcOEt 8:2) 0.43. An anal. sample was crystallized from MeCN/AcOEt. $[\alpha]_D^{25}$ = 142.3 (c = 0.65, $CHCl_3$). M.p. 157–159° (dec.). IR: 3570*m*, 2980*w*, 2920*m*, 2860*m*, 2200*w*, 2110*s*, 1670*m*, 1450*w*, 1340*w*, 1170*s*, 1100*s*, 1060*s*, 1030*s*, 1010*s*, 960*m*, 910*m*. ^{1}H-NMR ($CDCl_3$): 7.54–7.48 (*m*, 2 arom. H); 7.44–7.36 (*m*, 3 arom. H); 6.14 (*qd*, J = 1.7, 6.2, 1 olef. H)); 5.61 (*s*, PhC*H*)); 5.18 (*d*, J = 3.9, H–C(1)); 4.73 (*quint.*, J = 6.7, 1 olef. H)); 4.56 (*t*, J = 2.8, H–C(3)); 4.38 (*dd*, J = 5.2, 10.0, H_{eq}–C(6)); 4.28 (*dt*, J = 5.1, 9.9, H–C(5)); 3.75 (*t*, J = 10.1, H_{ax}–C(6)); 3.58 (*dd*, J = 2.7, 9.6, H–C(4)); 3.20 (*t*, J = 3.5, H–C(2)); 2.75–2.50 (br. *s*, exchanged with D_2O, OH); 1.70 (*dd*, J = 1.6, 6.9, Me). ^{13}C-NMR: 144.18 (*d*); 136.84 (*s*); 129.21 (*d*); 128.25 (*d*); 126.16 (*d*); 105.50 (*d*); 101.81 (*d*); 98.60 (*d*); 78.27 (*d*); 69.34 (*d*); 68.81 (*t*); 57.96 (*d*); 9.51 (*q*). CI-MS: 334 (25, $[M + 1]^+$), 306 (100), 248 (20). Anal. calc. for $C_{16}H_{19}N_3O_5$ (333.35): C 57.65, H 5.75, N 12.61; found: C 57.52, H 5.78, N 12.55.

*1,3,4,6-Tetra-*O*-acetyl-2-azido-2-deoxy-*D*-glucopyranose* (**5**). NaN_3 (8.00 g, 123.0 mmol) was dissolved at 23° in H_2O (20 ml) in a 100-ml three-neck round-bottom flask, equipped with a dropping funnel, a septum, and a N_2 balloon. CH_2Cl_2 (25 ml) was added to the vigorously stirred soln. at 0°. Tf_2O (freshly dist. over P_2O_5 under Ar, 4.1 ml, 25.0 mmol) was added within 30 min. The mixture was stirred for 2 h at 0°, the org. layer separated, and the aq. layer extracted with CH_2Cl_2 (2 × 10 ml). The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. (20 ml) and H_2O (20 ml), dried ($MgSO_4$), filtered, and the TfN_3 soln. was stored at 4° over 4-Å mol. sieves, c = 0.40M. A suspension of D-glucosamine hydrochloride (100 mg, 0.46 mmol) in MeOH (distilled over $Mg(OMe)_2$, 2 ml) was treated with a 0.5M soln. of NaOMe in MeOH (1.1 ml, 0.55 mmol) and stirred for 10 min at 26°. Dilution with MeOH (4.9 ml) and treatment with 4-(dimethylamino)pyridine (60 mg, 0.49 mmol) furnished a clear, colorless soln., to which the 0.40M TfN_3 soln. (3 ml, 1.2 mmol) was added at 26° within 10 min by syringe. After stirring for 18 h at 26° under N_2, the solvent was evaporated at 30° *i.v.* The oily, white suspension of the residue in anh. pyridine (3 ml) was treated at 0° with Ac_2O (2 ml) and stirred under N_2 for 4 h at this temp. It was diluted with CH_2Cl_2 (25 ml) and washed with 1M aq. HCl (2 × 25 ml). The combined aq. layers were extracted with CH_2Cl_2 (3 × 10 ml). The combined org. layers were washed with sat. aq. $NaHCO_3$ soln. (40 ml) and brine (40 ml), dried (Na_2SO_4) and concentrated *i.v.* FC (hexane/AcOEt 3:1) of the residue afforded 160 mg (91% from **4**) of **5**. Colorless oil. R_f (hexane/AcOEt 2:1) 0.33. $[\alpha]_D^{25}$ = +51.6 (c = 0.8, $CDCl_3$) ($[\alpha]_D^{20}$ of α-D-**5** = +130, β-D-**5** = +8, c = 1.0, $CHCl_3$ [3]). IR (film): 2118*s*, 1755*s*, 1432*w*, 1370*m*, 1220*s*, 1143*w*, 1110*w*, 1075*m*, 1050*m*. ^{1}H-NMR ($CDCl_3$): (α-D/β-D = 45:55); 6.25 (*d*, J = 3.7, 0.45 H, H–C(1)); 5.51 (*d*, J = 8.6, 0.55 H, H–C(1)); 5.41 (*dd*, J = 9.4, 10.4, 0.45 H, H–C(3)); 5.1–4.9 (*m*, 1.55 H, H–C(3), 2 H–C(4)); 4.24 (*dd*, J = 4.5, 12.4, 0.55 H, H–C(6)); 4.25 (*dd*, J = 4.1, 12.5, 0.45 H, H–C(6)); 4.04 (*dd*, J = 2.2, 12.4, 0.55 H, H'–C(6)); 4.12–3.98 (*m*, 0.9 H, H–C(5), H'–C(6)); 3.76 (*ddd*, J = 2.2, 4.5, 9.7, 0.55 H, H–C(5)); 3.62 (*dd*, J = 3.7, 10.5, 0.45 H, H–C(2)); 3.62 (*dd*, J = 8.6, 9.8, 0.55 H, H–C(2)); 2.15 (*s*, 1.35 H, AcO); 2.14 (*s*, 1.65 H, AcO); 2.06 (*s*, 1.35 H, AcO); 2.04 (*s*, 1.65 H, AcO); 2.03 (*s*, 3 H, 2 AcO); 2.00 (*s*, 1.35 H, AcO), 1.98 (*s*, 1.65 H, AcO). ^{13}C-NMR ($CDCl_3$): 170.35 (*s*); 169.67 (*s*); 169.60 (*s*); 169.46 (*s*); 169.38 (*s*); 168.38 (*s*); 168.34 (*s*); 92.4 (*d*); 89.84 (*d*); 72.57 (*d*); 70.63 (*d*); 69.63 (*d*); 67.83 (*d*); 67.74 (*d*); 62.48 (*d*); 61.32 (*t*); 60.18 (*d*); 20.70 (*q*); 20.68 (*q*); 20.46 (*q*); 20.35 (*q*).

*1,3,4,6-Tetra-*O*-acetyl-2-azido-2-deoxy-*D*-mannopyranose* (**7**). As described for **5**, **6** (100 mg, 0.46 mmol) was treated with a 0.5M soln. of NaOMe in MeOH (1.1 ml; 0.55 mmol), 4-(dimethylamino)pyridine (60 mg, 0.49 mmol), and a 0.40M TfN_3 soln. (3 ml, 1.2 mmol), followed by acetylation of the crude product, to give, after FC (hexane/AcOEt 3:1), 112 mg (65 %) of **7**. Colorless oil. R_f (hexane/AcOEt 2:1) 0.31. $[\alpha]_D^{25}$ = +40.8 (c = 1.5, $CDCl_3$) ($[\alpha]_D^{20}$ of α-D-**7** = +81.4, c = 1.0, $CHCl_3$) [5]). IR (film): 2117*s*, 1750*s*, 1430*w*, 1370*m*, 1220*s*, 1150*m*, 1090*m*(sh), 1050*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): (α-D/β-D = 76:24); 6.09 (*d*, J = 1.9, 0.76 H, H–C(1)); 5.81 (*d*, J = 1.4, 0.24 H, H–C(1)); 5.48–5.31 (*m*, 1.52 H, H–C(3), H–C(4)); 5.27 (*t*, J = 9.8, 0.24 H, H–C(4)); 5.04 (*dd*, J = 3.7, 9.8, 0.24 H, H–C(3)); 4.23 (*dd*, J = 4.9, 12.4, 0.24 H, H–C(6)); 4.21 (*dd*, J = 4.6, 12.4, 0.76 H, H–C(6)); 4.08 (*dd*, J = 2.2, 12.4, 0.76 H, H'–C(6)); 4.06 (*dd*, J = 2.4, 12.4, 0.24 H, H'–C(6)); 4.03–3.95 (*m*, 1 H, H–C(2), H–C(5)); 3.99 (*dd*, J = 1.9, 3.3, 0.76 H, H–C(2)); 3.70 (*ddd*, J = 2.4, 4.9, 9.9, 0.24 H, H–C(5)); 2.16 (*s*, 0.72 H, AcO); 2.13 (*s*, 2.28 H, AcO); 2.09 (*s*, 3 H, AcO); 2.07 (*s*, 2.28 H, AcO); 2.06 (*s*, 0.72 H, AcO); 2.03 (*s*, 2.28 H, AcO); 2.02 (*s*, 0.72 H, AcO). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.58 (*s*); 169.93 (*s*); 169.26 (*s*); 168.07 (*s*); 91.33 (*d*); 91.17 (*d*); 73.25 (*d*); 71.60 (*d*); 70.72 (*d*); 70.50 (*d*); 65.32 (*d*); 64.94 (*d*); 61.75 (*t*); 61.01 (*d*); 60.48 (*d*); 20.75 (*q*); 20.59 (*q*); 20.49 (*q*).

1,3,4,6-Tetra-O-acetyl-2-azido-2-deoxy-D-galactopyranose (**9**). As described for **5**, **8** (100 mg, 0.46 mmol) was treated with a 0.5M soln. of NaOMe in MeOH (1.1 ml, 0.55 mmol), 4-(dimethylamino)pyridine (60 mg, 0.49 mmol), and a 0.40M TfN_3 soln. (3 ml, 1.2 mmol), followed by acetylation of the crude product, to give, after FC (hexane/AcOEt 3:1), 122 mg (70%) of **9**. Colorless oil. R_f (hexane/AcOEt 2:1) 0.34. $[\alpha]_D^{25}$ = +36.7 (*c* = 1.6, $CDCl_3$) ($[\alpha]_D^{20}$ of α-D-**9** = +91.7, *c* = 1.05, $CHCl_3$ [2]). IR (film): 2120 s. ^{1}H-NMR ($CDCl_3$): (α-D/β-D= 40:60); 6.29 (*d*, *J* = 3.7, 0.4 H, H–C(1)); 5.51 (*d*, *J* = 8.5, 0.6 H, H–C(1)); 5.44 (*dd*, *J* = 1.3, 3.2, 0.4 H, H–C(4)); 5.34 (*dd*, *J* = 1.0, 3.4, 0.6 H, H–C(4)); 5.28 (*dd*, *J* = 3.2, 11.1, 0.4 H, H–C(3)); 4.86 (*dd*, *J* = 3.3, 10.8, 0.6 H, H–C(3)); 4.25 (*ddd*, *J* = 1.3, 6.6, 6.8, 0.4 H, H–C(5)); 4.15–4.02 (*m*, 2 H, 2 H–C(6), 2 H'–C(6)); 3.97 (*ddd*, *J* = 1.1, 6.1, 7.2, 0.6 H, H–C(5)); 3.90 (*dd*, *J* = 3.7, 11.1, 0.4 H, H–C(2)); 3.80 (*dd*, *J* = 8.5, 10.8, 0.6 H, H–C(2)); 2.16 (*s*, 1.8 H, AcO); 2.14 (*s*, 1.2 H, AcO); 2.13 (*s*, 3 H, AcO); 2.04 (*s*, 1.2 H, AcO); 2.03 (*s*, 1.8 H, AcO); 2.00 (*s*, 1.2 H, AcO); 1.99 (*s*, 1.8 H, AcO). ^{13}C-NMR (50 MHz, $CDCl_3$): 170.12 (*s*); 169.76 (*s*); 169.65 (*s*); 169.41 (*s*); 168.38 (*s*); 92.71 (*d*); 90.30 (*d*); 71.58 (*d*); 71.14 (*d*); 68.58 (*d*); 66.76 (*d*); 66.11 (*d*); 60.96 (*t*); 60.84 (*t*); 59.60 (*d*); 56.73 (*d*); 20.68 (*q*); 20.41 (*q*).

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