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Indium Mediated Allylation in Carbohydrate Chemistry: A Convenient Synthesis of 3-Deoxy-*D*-arabino-2-heptulosonic acid (*DAH*) and 3-Deoxy-*D*-arabino-2-heptulose (Kamusol)

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Summary. A short and economical synthesis of 3-deoxy-*D*-arabino-2-heptulosonic acid (**4**) and 3-deoxy-*D*-arabino-2-heptulose (kamusol, **8**) has been developed. In the key step of the reaction sequence, the indium mediated allylation of *D*-erythrose in an aqueous solvent system was utilized generating a seven carbon backbone which was further transformed into the title compounds.

Keywords. 3-Deoxy-*D*-arabino-2-heptulosonic acid; 3-Deoxy-*D*-arabino-2-heptulose (Kamusol); Indium mediated allylation.

Indiumunterstützte Allylierung in der Kohlenhydratchemie: Eine einfache Synthese von 3-Desoxy-*D*-arabino-2-heptulosonsäure (*DAH*) und 3-Desoxy-*D*-arabino-2-heptulose (Kamusol)

Zusammenfassung. Eine kurzer und ökonomischer Syntheseweg für 3-Desoxy-*D*-arabino-2-heptulosonsäure (**4**) und 3-Desoxy-*D*-arabino-2-heptulose (Kamusol, **8**) wurde entwickelt. Im Schlüsselschritt der Synthesesequenz wurde die indiumunterstützte Allylierung von *D*-Erythrose in wäßrigen Reaktionsmedien angewendet. Das mittels dieser Methode auf sieben Kohlenstoffatome verlängerte Kohlenhydrat-Grundgerüst konnte einfach in die Titelverbindungen übergeführt werden.

Introduction

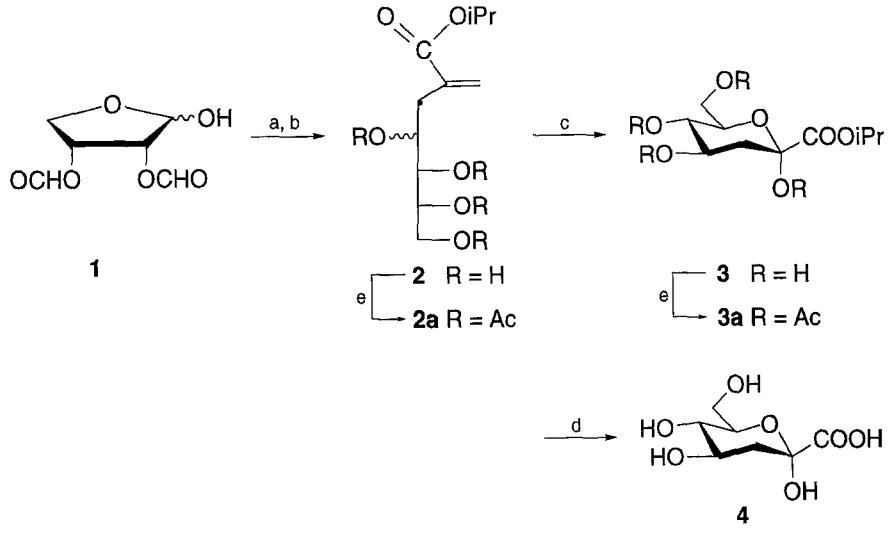
The increasing interest in synthetic approaches towards 3-deoxy-2-ulosonic acids such as sialic acids [1], 3-deoxy-*D*-manno-2-octulosonic acid (*KDO*, [2]), and 3-deoxy-*D*-arabino-2-heptulosonic acid 7-phosphate (*DAHP*, [3]) is due to their occurrence in various biological systems. Thus, the development of efficient synthetic strategies leading to this carbohydrates remains a challenging task. Furthermore, new strategies may open an access to analogues of these sugars with potential biological importance.

DAHP is a key intermediate in the shikimate pathway [3] leading from *D*-glucose to aromatic amino acids. A number of chemical [4–7] and chemo-enzymatic [8–10] syntheses of 3-deoxy-*D*-arabino-2-heptulosonic acid (*DAH*) and its 7-phosphorylated form *DAHP* as well as analogues thereof [11–13] have been reported. However, the multistep reaction sequences applied and the limited availability of the

enzymes utilized are drawbacks for an economical access to these α-keto acids. Here we report a short and convenient synthesis of *DAH* based on the indium mediated allylation of carbohydrates [14–17]. Furthermore, we demonstrate the broad possibility for the application of this methodology in the synthesis of 3-deoxy-*D*-arabino-2-heptulose (kamusol).

Results and Discussion

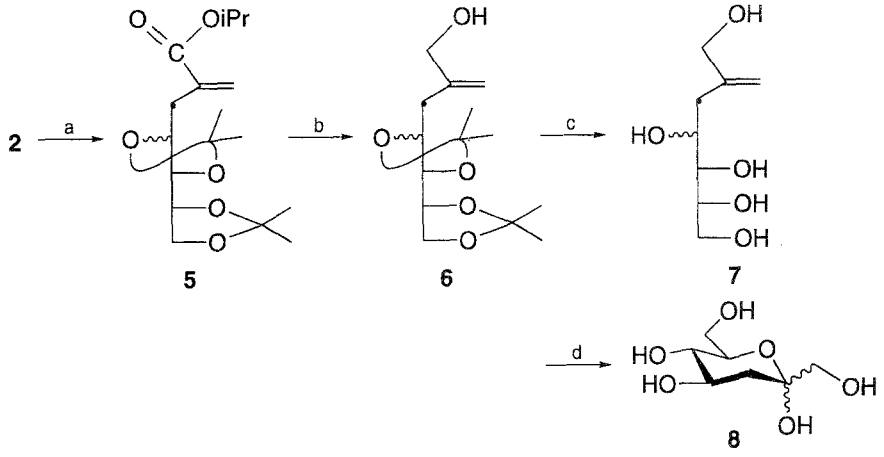
We started our reaction sequence towards *DAH* with *D*-erythrose which was freshly prepared from the readily available 2,3-di-O-formyl-*D*-erythrose derivative **1** [19] by acidic deprotection using Dowex 50W (H^+) cation exchange resin. Thus, treatment of *D*-erythrose with 3 equivalents of isopropyl 2-(bromomethyl)acrylate [20] and 1.1 equivalents of indium metal (Scheme 1) in a mixture of ethanol/water (4/1) under ultrasound promotion yielded a mixture of diastereomeric derivatives **2** (threo: erythro = 8:1). The mixture of diastereomers was used without separation for the subsequent ozonization to generate the desired *DAH* derivative **3** which could be easily separated by chromatography from its C-4 epimer. This result again confirms the observation that the major diastereomer generated in the course of the indium mediated allylation of unprotected carbohydrates exhibits a *threo* relationship between the newly generated hydroxyl function and that one originally present at C-2 of the starting aldehyde [14–17]. To simplify the structural assignment, compounds **2** and **3** were further transformed to their corresponding peracetylated derivatives **2a** and **3a**, respectively. The free heptulosonic acid **4** was obtained by saponification of the isopropyl ester of **3** utilizing sodium hydroxide.



Scheme 1. (a) Dowex 50 W, H^+; (b) isopropyl 2-(bromomethyl)acrylate, indium metal, ultrasound; (c) O_3, −78°C, Ph_3P; (d) NaOH, then H^+; (e) Ac_2O, pyridine, *DMAP*

To further demonstrate the synthetic potential of the heptulosonate backbone generated by indium mediated allylation, we prepared 3-deoxy-*D*-arabino-2-heptulose (kamusol, **8**). This seven carbon sugar was identified as metabolite isolated

from *Aspergillus sulphureus* [21]. We started our reaction sequence towards kamusol with the mixture of diastereomers **2**. Transformation of **2** to the corresponding diisopropyl derivatives **5** (Scheme 2) followed by reduction of the ester moiety with *DIBAH* made the heptulose precursor **6** accessible. The target compound kamusol (**8**) was readily obtained after acidic deprotection of **6** to the corresponding polyol system **7** followed by ozonization. **8** could be easily separated from its C-4 epimer by column chromatography over silica gel.



Scheme 2. (a) Acetone, $(CH_3)_2C(OCH_3)_2$, H^+; (b) *DIBAH*; (c) Dowex 50W, H^+; (d) O_3, $-78°C$, Ph_3P

In conclusion, we have developed a simple and convenient synthetic route towards the title compounds by utilizing the indium mediated allylation on unprotected carbohydrates in the key step of the reaction sequence. Since all transformations involved can be easily performed on a gram-scale, the synthetic approach presented opens an economical access to these biologically important carbohydrates.

Experimental

Chemicals were purchased from Aldrich and were of reagent grade. Analytical thin layer chromatography was performed on Merck plates (silica gel 60 F_{254}, 0.25 mm thick). Compounds were visualized by spraying with a solution of 3% $Ce(SO_4)_2$ in 2*N* H_2SO_4 followed by heating to 200 °C. Flash chromatography was performed using Merck silica gel 60 (0.04–0.063 mm). NMR spectra were recorded on Bruker AM 400 and AM 250 spectrometers (δ in ppm relative to internal *TMS*). Optical rotations were measured on a Perkin Elmer polarimeter 141. Abbreviations used are as follows: hexane (*PE*), ethyl acetate (*EA*), dichloromethane (*MC*), methanol (MeOH).

Isopropyl 2,3-dideoxy-2-C-methylen-D-arabino-heptulosonate (**2**)

To a solution of 2.088 g (11.85 mmol) of **1** [19] in 5 ml of water, 1 g of Dowex 50W (H^+) was added and the solution was kept at 60 °C for 3 h. The resin was filtered off and the filtrate was diluted with 20 ml of ethanol. To this solution, pieces of indium metal (1.486 g; 1.1 equiv.) as well as 4.6 ml of isopropyl 2-(bromomethyl)acrylate (3 equiv.) were added, and the reaction mixture was sonicated until no more starting material could be detected (TLC: *MC*:MeOH = 8:1). The solvent was removed under reduced

pressure, and the crude material obtained was purified by flash chromatography over silica gel (*MC*: MeOH = 9:1) to yield 2.681 g (91%) of an inseparable mixture of C-4 epimers (*threo*:*erythro* = 8:1) as a colorless foam.

^{1}H NMR (major diastereomer; *DMSO*-d_6, 5% D_2O): δ = 1.20 (d, 6H, J = 6.32 Hz, 2 × CH_3), 2.38 (d, J = 6.6 Hz, 2H, H-3a, H-3b), 3.10 (ddd, J = 7.4 Hz, J = 7.1 Hz, 1H, H-6), 3.30–3.60 (m, J = 2.5 Hz, 1H, H-7), 3.82 (dd, J = 6.6 Hz, J = 7.4 Hz, 1H, H-4), 4.08 (dd, J = 7.4 Hz, 1H, H-5), 4.31 (dd, J = 4.9 Hz, J = 12.1 Hz, 1H, H-7), 4.91 (m_c, 1H, $CH(CH_3)_2$), 5.61 (d, 1H, H-2a), 6.03 (d, 1H, H-2b); ^{13}C NMR *DMSO*-d_6, 5% D_2O): δ = 21.49 ($C(CH_3)_2$), 36.15 (C-3), 63.55 (C-7), 67.34, 67.64, 71.23, 72.43, (C-4, C-5, C-6, $C(CH_3)_2$), 126.05, 138.22, (C-2, C-2'), 166.02 (CO).

Isopropyl 4,5,6,7-tetra-O-acetyl-2,3-dideoxy-2-C-methylen-D-arabino-heptulosonate (**2a**)

To a solution of 248 mg of **2** in 3.5 ml of dry pyridine, 2.5 ml of acetic anhydride and 5 mg of N,N-dimethylamino pyridine (*DMAP*) were added. The reaction mixture was stirred at room temperature for 12 h. After removal of the solvents *in vacuo*, the residue was purified by flash chromatography over silica gel (*EA*:*PE* = 1:1) to yield 314 mg (75%) of **2a** as a yellowish foam.

^{1}H NMR ($CDCl_3$): δ = 1.20–1.35 (m, 6H, 2 $C(CH_3)_2$), 1.90–2.10 (4s, 12H, 4 CH_3), 2.28 (dd, $J_{3a,4}$ = 9.9 Hz, $J_{3a,3b}$ = 13.8 Hz, 1H, H-3a), 2.59 (dd, $J_{3b,4}$ = 3.6 Hz, 1H, H-3b), 4.08 (dd, $J_{6,7a}$ = 4.9 Hz, $J_{7a,7b}$ = 12.4 Hz, 1H, H-7a), 4.16 (dd, $J_{6,7b}$ = 2.8 Hz, 1H, H-7b), 4.95–5.10 (m, 2H, H-6, $CH(CH_3)_2$), 5.26 (dd, $J_{4,5}$ = 2.8 Hz, $J_{5,6}$ = 10.7 Hz, 1H, H-5), 5.40 (dddd, 1H, H-4), 5.49 (s, 1H, =CH), 6.16 (d, 1H, =CH); ^{13}C NMR ($CDCl_3$): δ = 20.45, 20.56, 21.50, 21.55 (6 × CH_3), 34.15 (C-3), 61.68 (C-7), 68.21, 68.60, 69.77, 70.33 (C-4, C-5, C-6, $CH(CH_3)_2$), 127.42, 135.91 (C-2, C-2'), 165.33, 166.27, 169.60, 170.38 (CO); $C_{19}H_{28}O_{10}$ (416.43); calcd.: C 54.80, H 6.70; found: C 54.91, H 6.84.

Isopropyl 3-deoxy-D-arabino-heptulosonate (**3**)

A stirred solution of 423 mg (1.70 mmol) of **3** in 30 ml of a mixture of *MC*/MeOH (1/1) was cooled to −78 °C, and ozone was bubbled through the reaction mixture until a blue color remained. The excess of ozone was removed by dropwise addition of a 10% solution of triphenylphosphine in *MC* until a colorless solution was obtained. The solvent was removed under reduced pressure and the crude material obtained purified by flash chromatography over silica gel (eluent: *MC*:MeOH = 8:1). Yield: 203 mg (48%) of **3** as a colorless foam.

$[\alpha]_D^{20}$ = 14.4° (c = 0.88, H_2O); ^{1}H NMR (D_2O): δ = 1.25 (2d, J = 6.3 Hz, 6H, 2 × CH_3), 1.80 (dd, $J_{3ax,3eq}$ = 12.6 Hz, $J_{3ax,4}$ = 12.4 Hz, 1H, H-3_{ax}) 2.22 (dd, $J_{3eq,4}$ = 5.2 Hz, 1H, H-3_{eq}), 3.40 (dd, $J_{5,6}$ = 9.6 Hz, $J_{4,5}$ = 9.4 Hz, 1H, H-5), 3.60–3.85 (m, 3H, H-6, H-7a, H-7b), 3.95 (ddd, 1H, H-4), 5.07 (qq, J = 6.3 Hz, 1H, $CH(CH_3)_2$); ^{13}C NMR (D_2O): δ = 20.99 (2 × CH_3), 38.87 (C-3), 68.71, 70.49, 72.38, 74.38 (C-4, C-5, C-6, $CH(CH_3)_2$), 95.43 (C-2), 170.94 (CO).

Isopropyl 2,4,5,7-tetra-O-acetyl-3-deoxy-D-arabino-heptulosonate (**3a**)

42 mg (0.16 mmol) of **3** were treated analogously to compound **2a**. After flash chromatography over silica gel (eluent: *PE*:*EA* = 5:1), 52 mg (78%) of **3a** were obtained as a colorless foam.

$[\alpha]_D^{20}$ = 37.7° (c = 0.22, $CHCl_3$); ^{1}H NMR ($CDCl_3$): δ = 1.22 (2 d, J = 6.3 Hz, 6H, $CH(CH_3)_2$), 1.99–2.03 (m, 13H, 4 × CH_3, H-3_{ax}), 2.60 (dd, $J_{3eq,4}$ = 5.2 Hz, $J_{3ax,3eq}$ = 13.5 Hz, 1H, H-3_{eq}), 3.95 (ddd, $J_{5,6}$ = 9.9 Hz, $J_{6,7a}$ = 2.2 Hz, $J_{6,7b}$ = 4.1 Hz, 1H, H-6), 4.08 (dd, 1H, $J_{7a,7b}$ = 12.2 Hz, 1H, H-7a), 4.30 (dd, 1H, H-7b), 5.02 (qq, 1H, $CH(CH_3)_2$), 5.08 (dd, $J_{4,5}$ = 9.6 Hz, 1H, H-5), 5.25 (ddd, 1H, H-4); ^{13}C NMR ($CDCl_3$): δ = 20.59, 20.79, 21.31, 21.40 (6 × CH_3), 35.39 (C-3), 61.70 (C-7), 68.25, 68.45, 70.39, 71.37 (C-4, C-5, C-6, $CH(CH_3)_2$), 97.36 (C-2), 165.10, 168.18, 169.56, 170.11, 170.69 (CO); $C_{18}H_{26}O_{11}$ (418.40); calcd.: C 51.67, H 6.26; found: C 51.84, H 6.41.

3-Deoxy-D-arabino-heptulosonic acid (**4**)

To a solution of 200 mg (0.80 mmol) of **3** in 5 ml of MeOH, 40 mg of solid NaOH were added. After all the starting material has disappeared (TLC: *MC*:MeOH = 16:3), the reaction mixture was neutralized with Dowex 50W (H^+). The resin was filtered off and the solvent was removed *in vacuo* to obtain 138 mg (83%) of **4** as a colorless glass.

^{1}H NMR (D_2O): $\delta = 1.77$ (dd, $J_{3ax,4} = 12.1$ Hz, $J_{3ax,eq} = 13.2$ Hz, 1H, H-3_{ax}), 2.20 (dd, $J_{3eq,4} = 4.9$, 1H, H-3_{eq}), 3.70–4.00 (m, 5H, H-4, H-5, H-6, H-7a, H-7b); ^{13}C NMR (D_2O): $\delta = 39.44$ (C-3), 60.33 (C-7), 69.08, 70.73, 73.82 (C-4, C-5, C-6), 96.88 (C-2), 176.66 (C-1).

Isopropyl 4,5:6,7-di-O-isopropylidene-2,3-dideoxy-2-C-methylene-D-arabino-heptulosonate (**5**)

To a solution of 659 mg (2.65 mmol) of **2** in 20 ml of dry acetone, 5 ml of 2,2-dimethoxypropane and 10 mg of *p*-toluenesulfonic acid monohydrate were added and the reaction mixture was stirred for 3 h at room temperature. The solvent was removed under reduced pressure; the crude material obtained was purified by flash chromatography over silica gel (eluent: *EA*:*PE* = 4:1). Yield: 329 mg (38%) as a colorless foam.

^{1}H NMR (major diastereomer; $CDCl_3$): $\delta = 1.24$, 1.27, 1.31, 1.33, 1.36, 1.39 (4s, m, 18H, 6 × CH_3), 2.48 (dd, $J_{3a,3b} = 15.1$ Hz, $J_{3a,4} = 8.5$ Hz, 1H, H-3a), 2.83 (ddd, 1H, $J = 0.9$ Hz, $J_{3b,4} = 3.6$ Hz, H-3b), 3.60 (dd, $J = 7.4$ Hz, 1H, H-5), 3.92 (dd, $J_{7a,7b} = 7.4$ Hz, $J_{6,7a} = 4.7$ Hz, 1H, H-7a), 3.98–4.16 (m, 3H, H-4, H-6, H-7b), 5.05 (m, 1H, $CH(CH_3)_2$), 5.67 (dd, $J = 1.38$ Hz, 1H, =CH); 6.21 (d, 1H, =CH); ^{13}C NMR ($CDCl_3$): $\delta = 21.75$ ($2CH_3$), 25.46, 26.56, 26.74, 27.02 ($4CH_3$), 35.92 (C-3), 67.47 (C-7), 68.02, 76.93, 78.42, 80.87 (C-4, C-5, C-6, $CH(CH_3)_2$), 109.16, 109.55 ($2C(CH_3)_2$), 128.11; 137.39 (C-2, C-2); $C_{17}H_{28}O_6$ (328.41); calcd.: C 62.18, H 8.59; found: C 62.62, H 8.78.

4,5:6,7-Di-O-isopropylidene-2,3-dideoxy-2-C-methylene-D-arabino-heptitol (**6**)

A solution of 292 mg (0.89 mmol) of **5** in 10 ml of dry toluene was cooled to −78 °C. 1.1 ml of a 1 *N* solution of diisobutyl aluminiumhydride (1.2 equiv.) were added under constant stirring. After a reaction time of 1 h, 3 ml of MeOH and 5 ml of a 10% solution of potassium sodium *L*-tartrate were added and the solution was stirred at room temperature for 16 h. The organic layer was separated and the aqueous phase was extracted three times with 15 ml of *EA*. The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed under reduced pressure. After passing the almost pure material obtained over 5 g of silica gel (eluent: *PE*:*EA* = 7:3), 293 mg (98%) of **6** were isolated.

^{1}H NMR (major diastereomer; $CDCl_3$): $\delta = 2.34$ (dd, $J_{3a,3b} = 14.8$ Hz, $J_{3a,4} = 8.8$ Hz, 1H, H-3a), 2.64 (dd, $J_{3b,4} = 2.5$ Hz, 1H, H-3b), 3.57 (dd, $J = 8.0$ Hz, $J = 7.7$ Hz, 1H, H-5), 3.66 (d, $J = 7.4$ Hz, 1H, H-1), 3.93 (dd, $J_{7a,7b} = 8.0$ Hz, $J_{6,7a} = 4.7$ Hz, 1H, H-7a), 3.98–4.15 (m, 4H, H-1, H-6, H-7b, H-4), 4.98 (d, $J = 0.55$ Hz, 1H, =CH), 5.10 (s, 1H, =CH); ^{13}C NMR ($CDCl_3$): $\delta = 25.10$, 26.49, 26.59, 26.79, (4 × CH_3), 37.30 (C-3), 66.09, 67.77 (C-1, C-7), 76.89, 76.90, 80.65 (C-4, C-5, C-6), 109.04, 109.60 ($2C(CH_3)_2$), 113.38, 145.41 (C-2, C-2′); $C_{14}H_{24}O_5$ (272.34); calcd.: C 61.74, H 8.88; found: C 61.47, H 9.13.

2,3-Dideoxy-2-C-methylene-D-arabino-heptitol (**7**)

To a solution of 205 mg (0.75 mmol) of **6** in 5 ml of a mixture of MeOH/H_2O (9/1), 0.5 ml of a 1 *N* HCl solution were added. The reaction mixture was stirred at 60 °C for 3 h and then neutralized with solid sodium bicarbonate. The solvents were removed *in vacuo*, and the crude material obtained was purified by flash chromatography over silica gel (eluent: *MC*:MeOH = 8:1) to yield 82 mg (57%) of **7**.

^{1}H NMR (major diastereomer; D_2O): $\delta = 2.28$ (2s, 2H, 2 × H-3), 3.33 (dd, $J_{1a,1b} = 7.4$ Hz, $J = 1.4$ Hz, 1H, H-1a), 3.55 (dd, $J_{6,7a} = 5.5$ Hz, $J_{7a,7b} = 10.5$ Hz, 1H, H-7a), 3.63 (ddd, $J_{5,6} = 8.8$ Hz, 1H, H-6), 3.71 (dd, 1H, $J_{6,7b} = 3.0$ Hz, H-7b), 3.95 (dd, $J = 1.7$ Hz, 1H, H-1b), 3.96–4.01 (m, 2H, H-4, H-5);

^{13}C NMR (D_2O): δ = 39.1 (C-3), 65.38, 66.60 (C-1, C-7), 70.43, 73.62, 74.34 (C-4, C-5, C-6), 113.2, 148.0 (C-2, C-2′).

3-Deoxy-D-arabino-heptulose (**8**)

A solution of 82 mg (0.43 mmol) of **7** in 10 ml of a mixture of *MC*/MeOH (1/1) was treated with ozone as described for compound **3**. After removal of the solvent under reduced pressure, pure **8** was obtained after flash chromatography over silica gel (eluent: *MC*:MeOH = 9:1).

Yield: 47 mg (56%); $[\alpha]_D^{20}$ = 25.7 → 24.0° (48 h; c = 0.42, H_2O); ^{1}H NMR (methanol-d_4): δ = 1.70 (dd, J = 11.8 Hz, J = 13.75 Hz, 1H, H-3_{ax}), 2.08 (dd, J = 5.2 Hz, 1H, H-3_{eq}), 3.3–4.0 (m, 7H, 2 H-1, H-4, H-5, H-6, 2 H-7); ^{13}C NMR (methanol-d_4): δ = 37.05 (C-3), 62.55, 64.57 (C-1, C-7), 70.14, 72.36, 75.24 (C-4, C-5, C-6), 105.96 (C-2).

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References

[1] (a) Schauer R (1982) Sialic acids. Springer Verlag, Wien
(b) Schauer R (1982) Adv Carbohydr Chem Biochem **40**: 131
[2] Unger FM (1981) Adv Carbohydr Chem Biochem **38**: 323
[3] Haslam E (1974) The Shikimate Pathway. Butterworth, London
[4] Johnson CR, Kozak J (1994) J Org Chem **59**: 2910
[5] Lopez-Herrera FJ, Sarabia-Garcia F (1994) Tetrahedron Lett **35**: 6705
[6] Ramage R, MacLeod AM, Rose GW (1991) Tetrahedron **47**: 5625
[7] Dondoni A, Marra A, Merino P (1994) J Am Chem Soc **116**: 3324
[8] Reimer LM, Conley DL, Pompliano DL, Frost JW (1986) J Am Chem Soc **108**: 8010
[9] (a) Garner CC, Herrmann KM (1984) Carbohydr Res **132**: 317
(b) Sugai T, Shen G-J, Ichikawa Y, Wong C-H (1993) J Am Chem Soc **115**: 413
[10] Augé C, Delest V (1995) Tetrahedron Asymm **6**: 863
[11] Horton D, Nickol RG, Varela O (1987) Carbohydr Res **168**: 295
[12] Banaszek A (1995) Tetrahedron **51**: 4231
[13] Devianne G, Escudier J-M, Baltas M, Gorrichon L (1995) J Org Chem **60**: 7343
[14] (a) Binder WH, Prenner WH, Schmid W (1994) Tetrahedron **50**: 749
(b) Prenner RH, Binder WH, Schmid W (1994) Liebigs Ann Chem 73
[15] (a) Chen T-H, Lee M-C (1995) J Org Chem **60**: 4228
(b) Chen T-H, Li C J (1992) J Chem Soc Chem Commun: 747
[16] (a) Gordon DM, Whitesides GM (1993) J Org Chem **58**: 7937
(b) Gao J, Härter R, Gordon DM, Whitesides GM (1994) J Org Chem **59**: 3714
[17] Kim E, Gordon DM, Schmid W, Whitesides GM (1993) J Org Chem **58**: 5500
[18] Cintas P (1995) Synlett: 1087
[19] Perlin AS (1962) Methods Carbohydr Chem **1**: 64
[20] Villieras J, Rambaud M (1987) Org Synth **66**: 220
[21] Kamal A, Haider Y, Akhtar R, Quereshi AS (1971) Pak J Sci Ind Res **14**: 63; (1971) Chem Abstr **75**: 126859d

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