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Supporting Information

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Oxidative Cleavage of 3-Alkoxy-2,5-dihydrofurans and its Application to the *de Novo* Synthesis of Rare Monosaccharides Exemplified by L-Cymarose

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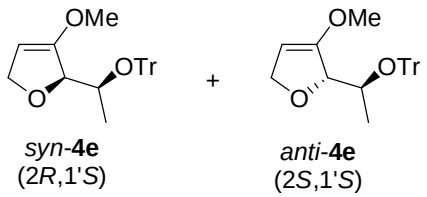
(2*R*,1'*S*)-3-Methoxy-2-(1-trityloxyethyl)-2,5-dihydrofuran and **(2*S*,1'*S*)-3-Methoxy-2-(1-trityloxyethyl)-2,5-dihydrofuran** *syn*/*anti*-**(4e)**



syn-**4e** (2*R*,1'*S*) *anti*-**4e** (2*S*,1'*S*)

Methoxyallene (7.00 mL, 5.88 g, 83.9 mmol) was dissolved in Et_2O (150 mL), precooled to -45 °C. A solution of *n*-BuLi (2.50 M in hexanes, 31.0 mL, 77.5 mmol) was slowly added and the mixture was stirred for 20 min. The mixture was cooled to -78 °C and a solution of aldehyde **13**[1] (7.71 g, 24.4 mmol) in Et_2O (100 mL) was added over 10 min with the aid of a double-tip needle. The mixture was stirred at -78 °C for 5 h. Then, H_2O (100 mL) was added and the mixture was warmed to r.t. The layers were separated and the aqueous layer was extracted with Et_2O (3 × 100 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated to dryness. The crude product was dried at 0.1 mbar to provide 9.91 g (quant.) of the allene adduct as an orange oil. ^{1}H-NMR showed a *syn*/*anti*-ratio of 30:70. Tentative assignment of the diastereomers was based on the Felkin-Anh transition state model.

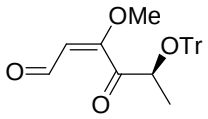
syn-adduct: ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.91 (d, *J* = 6.3 Hz, 3 H, 1-H), 2.57 (d, *J* = 7.2 Hz, 1 H, OH), 3.28 (s, 3 H, OMe), 3.60 (m_c, 1 H, 2-H), 3.95 (m_c, 1 H, 3-H), 5.53-5.55 (br. m, 2 H, 6-H), 7.20-7.31, 7.47-7.53 (2 m, 15 H, Ph) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 15.2 (q, C-1), 56.0 (q, OMe), 71.2 (d, C-3), 72.0 (d, C-2), 86.7 (s, CPh_3), 92.4 (t, C-6), 127.01, 127.6, 129.0 (3 d, Ph), 134.3 (s, C-4), 145.0 (s, Ph), 198.4 (s, C-5) ppm. *anti*-adduct: ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.02 (d, *J* = 6.3 Hz, 3 H, 1-H), 2.25 (d, *J* = 5.0 Hz, 1 H, OH), 3.28 (s, 3 H, OMe), 3.55 (m_c, 1 H, 3-H), 3.83 (dq, *J* = 3.6, 6.3 Hz, 1 H, 2-H), 5.52 (br. t, *J* = 2.9 Hz, 2 H, 6-H), 7.20-7.31, 7.47-7.53 (2 m, 15 H, Ph) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 15.6 (q, C-1), 55.9 (q, OMe), 71.5 (d, C-3), 74.5 (d, C-2), 87.1 (s, $\underline{C}Ph_3$), 92.6 (t, C-6), 127.02, 127.7, 128.9 (3 d, Ph), 134.4 (s, C-4), 144.8 (s, Ph), 197.9 (s, C-5) ppm.

The crude adduct (9.91 g, max. 24.4 mmol) was dissolved in DMSO (100 mL), with careful exclusion of oxygen. The solution was warmed to 60 °C and a solution of KO*t*-Bu (1.42 g, 12.7 mmol) in DMSO (20 mL) was slowly added, whereupon the mixture turned black. After 90 min at 60 °C, the mixture was cooled to r.t. and $NaHCO_3$-solution (sat. aq., 100 mL) and H_2O (50 mL) were added with vigorous stirring. The mixture was extracted with CH_2Cl_2 (4 × 200 mL). The combined organic layers were washed with H_2O and brine, dried with $MgSO_4$, filtered and concentrated. Column chromatography (silica gel, EtOAc/hexane = 1:10) provided 8.09 g (86% over 2 steps) *syn*/*anti*-**4e** as sticky orange oil. ^{1}H-NMR of the purified product showed unaltered *d.r.* A sample of the product was subjected to HPLC separation for analysis.

syn-**4e**: Yellow sticky oil, $[\alpha]_D^{22}$ = –20.1 (c = 1.41, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.82 (d, *J* = 6.4 Hz, 3 H, 2'-H), 3.59 (dq, *J* = 2.8, 6.4 Hz, 1 H, 1'-H), 3.62 (s, 3 H, OMe), 4.25 (m_c, 1 H, 2-H), 4.59-4.63 (m, 1 H, 4-H), 4.69-4.74 (m, 2 H, 5-H), 7.19-7.33, 7.50-7.53 (2 m, 15 H, Ph) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 16.6 (q, C-2'), 57.3 (q, OMe), 70.7 (d, C-1'), 73.4 (t, C-5), 84.2 (d, C-2), 86.3 (s, $\underline{C}Ph_3$), 91.4 (d, C-4), 127.5, 127.9, 129.1 (3 d, Ph), 145.3 (s, Ph), 156.5 (s, C-3) ppm. *anti*-**4e**: Yellow sticky oil, $[\alpha]_D^{22}$ = +25.0 (c = 1.99, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 0.81 (d, *J* = 6.5 Hz, 3 H, 2'-H), 3.51 (s, 3 H, OMe), 3.84 (dq, *J* = 1.8, 6.5 Hz, 1 H, 1'-H), 4.17 (ddd, *J* = 1.8,

3.4, 6.5 Hz, 1 H, 2-H), 4.54 (q, *J* = 1.8 Hz, 1 H, 4-H), 4.59-4.65 (m, 2 H, 5-H), 7.19-7.30, 7.52-7.55 (2 m, 15 H, Ph) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 14.4 (q, C-2'), 57.4 (q, OMe), 71.3 (d, C-1'), 73.7 (t, C-5), 84.5 (d, C-2), 86.9 (s, $\underline{C}Ph_3$), 90.9 (d, C-4), 126.8, 127.6, 129.2 (3 d, Ph), 145.1 (s, Ph), 156.3 (s, C-3) ppm. *syn*/*anti*-**4e**: IR (film): ν = 3090-2850 cm^{-1} (=C-H, –C-H), 1660, 1600 (C=C). MS (FAB+): *m*/*z* (%) = 409 ([M + Na]$^+$, 3), 243 ([CPh_3]$^+$, 100). Anal. calc. for $C_{26}H_{26}O_3$ (386.5): C 80.80, H 6.78, found: C 80.80, H 6.90.

(5*S*)-3-Methoxy-4-oxo-5-trityloxyhex-2-enal (6e)



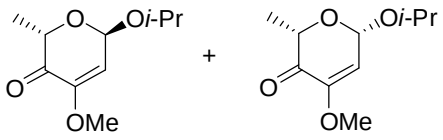
6e

H_2O (8.00 mL) was suspended in a solution of *syn*/*anti*-**4e** (9.14 g, 23.6 mmol) in CH_2Cl_2 (130 mL). Then, DDQ (10.7 g, 47.1 mmol) was added in one portion and the mixture was vigorously stirred at r.t. for 2 h. $NaHCO_3$-solution (sat. aq., 100 mL) and H_2O (50 mL) were added and the mixture was further stirred for 10 min. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated. Column chromatography (silica gel, EtOAc/hexane = 1:3 ? 1:2) provided **6e** as a sticky yellow resin, that was extensively dried at 0.1 mbar to afford 7.85 g (83%) of a yellow amorphous solid. Chiral phase HPLC analysis of this material, compared to a racemic reference sample, revealed *e.r.* > 99:1 (conditions: Chiralpak AD column, Daicel Chemical Industries Ltd., hexane/*i*-PrOH = 100:0 ? 98:2 over 40 min, flow 1 mL/min, 18 bar. Retention time: (*R*)-enantiomer 23.1 min, (*S*)-enantiomer 33.6 min. Detection: UV, λ = 254 nm).

m.p. 119-121 °C. $[\alpha]_D^{22}$ = –122.7 (c = 1.51, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.41 (d, *J* = 6.7 Hz, 3 H, 6-H), 3.58 (s, 3 H, OMe), 4.80 (q, *J* = 6.7 Hz, 1 H, 5-H), 5.20 (d, *J* = 7.0 Hz, 1 H, 2-H), 7.20-7.29, 7.44-7.47 (2 m, 15 H, Ph), 9.45 (d, *J* = 7.0 Hz,

1 H, 1-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 19.2 (q, C-6), 55.9 (q, OMe), 72.1 (d, C-5), 87.9 (s, $\underline{C}Ph_3$), 109.8 (d, C-2), 127.4, 128.0, 129.0 (3 d, Ph) 143.9 (s, Ph), 164.6 (s, C-3), 191.6 (s, C-4), 197.6 (s, C-1) ppm. IR (KBr): ν = 3090-2900 cm^{-1} (=C-H, –C-H), 1660 (C=O). MS (EI, 80 eV, 140 °C): *m*/*z* (%) = 400 ($[M]^+$, < 1), 243 ($[CPh_3]^+$, 100), 165 (39). Anal. calc. for $C_{26}H_{24}O_4$ (400.5): C 77.98, H 6.04, found: C 77.80, H 5.80.

(2*S*,6*R*)-6-Isopropoxy-4-methoxy-2-methyl-6*H*-pyran-3-one and **(2*S*,6*S*)-6-Isopropoxy-4-methoxy-2-methyl-6*H*-pyran-3-one** *a*/*b*-**(15)**



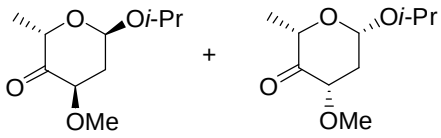
a-**15** *b*-**15**

Ketoaldehyde **6e** (7.86 g, 19.6 mmol) and $HC(O\textit{i}\text{-}Pr)_3$ (7.41 g, 38.9 mmol) were dissolved in CH_2Cl_2 (50 mL). A solution of iodine (1.52 g, 5.99 mmol) in *i*-PrOH (100 mL) was added and the mixture was heated to 60 °C for 2.5 h (no argon). After cooling to r.t., NaOH-solution (2.50 M aq., 6 mL) was added and stirring was continued for 10 min. The mixture was poured into a solution of $Na_2S_2O_3$ (sat. aq., 100 mL) mixed with $NaHCO_3$-solution (sat. aq., 100 mL), and washed. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (4 × 150 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated. Column chromatography (silica gel, EtOAc/hexane = 1:3) provided 3.52 g (90%) *a*/*b*-**15** as a yellowish liquid which solidified to a wax upon storage in the refrigerator. Due to its volatility, the product was cooled in an ice-bath when dried in vacuo. ^{1}H-NMR of the crude and purified products showed an *a*/*b*-ratio of 83:17. A sample of the product was subjected to HPLC separation which provided only *a*-**15** in anomerically pure form.

a-**15**: Colorless solid, m.p. 47 °C. $[\alpha]_D^{22}$ = –42.4 (c = 0.25, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.23, 1.27 (2 d, *J* = 6.2 Hz, 2 × 3 H, *i*-Pr), 1.41 (d, *J* = 6.8 Hz, 3 H, CH_3), 3.64 (s, 3 H, OMe), 4.03 (hept., *J* = 6.2 Hz, 1 H, *i*-Pr), 4.66 (q, *J* = 6.8 Hz, 1 H, 2-H), 5.46

(d, *J* = 4.2 Hz, 1 H, 6-H), 5.70 (d, *J* = 4.2 Hz, 1 H, 5-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 15.4 (q, CH_3), 21.9, 23.2 (2 q, *i*-Pr), 54.9 (q, OMe), 70.49 (d, C-2), 70.54 (d, *i*-Pr), 93.0 (d, C-6), 111.1 (d, C-5), 149.7 (s, C-4), 192.8 (s, C-3) ppm. *b*-**15**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.24, 1.29 (2 d, *J* = 6.2 Hz, 2 × 3 H, *i*-Pr), 1.50 (d, *J* = 6.7 Hz, 3 H, CH_3), 3.65 (s, 3 H, OMe), 4.14 (hept., *J* = 6.2 Hz, 1 H, *i*-Pr), 4.18 (dq, *J* = 1.1, 6.7 Hz, 1 H, 2-H), 5.54 (dd, *J* = 1.1, 2.0 Hz, 1 H, 6-H), 5.75 (d, *J* = 2.0 Hz, 1 H, 5-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.0 (q, CH_3), 21.7, 23.5 (2 q, *i*-Pr), 55.0 (q, OMe), 70.6 (d, *i*-Pr), 74.8 (d, C-2), 95.0 (d, C-6), 114.3 (d, C-5), 150.2 (s, C-4), 192.8 (s, C-3) ppm. *a*/*b*-**15**: IR (film): ν = 3070-2840 cm^{-1} (=C-H, –C-H), 1710 (C=O). MS (EI, 80 eV, 30 °C): *m*/*z* (%) = 200 ([M]$^+$, 19), 158 (19), 141 ([M – C_3H_7O]$^+$, 100), 114 (46), 71 (38), 57 (39). HRMS (EI, 80 eV, 30 °C): *m*/*z* calc. for $C_{10}H_{16}O_4$: 200.1049, found: 200.1052.

(2*S*,4*R*,6*R*)-6-Isopropoxy-4-methoxy-2-methyldihydropyran-3-one (16) and **(2*S*,4*S*,6*S*)-6-Isopropoxy-4-methoxy-2-methyldihydropyran-3-one (17)**

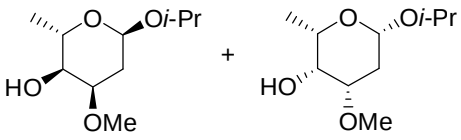


16 **17**

Rhodium on Al_2O_3 (5 weight-%, 637 mg, 0.31 mmol) was suspended in EtOAc (30 mL), under an atmosphere of argon. Then, the catalyst was saturated with hydrogen, *via* a cannula, over 30 min. A solution of *a*/*b*-**15** (611 mg, 3.05 mmol) in EtOAc (15 mL) was added and stirring was continued at r.t. and 1 bar hydrogen pressure for 4.5 h. The suspension was filtered through a pad of celite with the aid of EtOAc and the filtrate was concentrated. ^{1}H-NMR of the crude product mixture showed two diastereomers (*d.r.* > 95:5 each). Column chromatography (silica gel, EtOAc/hexane = 1:2) provided 414 mg (67%) of a mixture of **16** and **17**, as a colorless solid (ratio 81:19 by ^{1}H-NMR). Due to its volatility, the product mixture was cooled in an ice-bath when dried in vacuo. A sample of the product was subjected to HPLC separation which provided only **16** in pure form.

16: Yellowish solid, m.p. 44 °C. $[\alpha]_D^{22}$ = –252.1 (c = 0.36, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.16, 1.20 (2 d, *J* = 6.2 Hz, 2 × 3 H, *i*-Pr), 1.33 (d, *J* = 7.0 Hz, 3 H, CH_3), 1.80 (ddd, *J* = 6.6, 13.1, 13.6 Hz, 1 H, 5-H), 2.68 (ddd, *J* = 6.6, 6.7, 13.6 Hz, 1 H, 5-H), 3.47 (s, 3 H, OMe), 3.94 (hept., *J* = 6.2 Hz, 1 H, *i*-Pr), 4.09 (ddd, *J* = 0.7, 6.7, 13.1 Hz, 1 H, 4-H), 4.39 (q, *J* = 7.0 Hz, 1 H, 2-H), 5.19 (t, *J* = 6.6 Hz, 1 H, 6-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 15.7 (q, CH_3), 21.6, 23.5 (2 q, *i*-Pr), 34.1 (t, C-5), 58.2 (q, OMe), 69.2 (d, *i*-Pr), 71.3 (d, C-2), 77.2 (d, C-4), 94.73 (d, C-6), 211.5 (s, C-3) ppm. **17**: ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.18, 1.23 (2 d, *J* = 6.2 Hz, 2 × 3 H, *i*-Pr), 1.25 (d, *J* = 6.5 Hz, 3 H, CH_3), 2.06 (dt, *J* = 3.6, 12.4 Hz, 1 H, 5-H), 2.47 (ddd, *J* = 1.5, 6.6, 12.4 Hz, 1 H, 5-H), 3.48 (s, 3 H, OMe), 3.95 (hept., *J* = 6.2 Hz, 1 H, *i*-Pr), 4.22 (dd, *J* = 6.6, 12.4 Hz, 1 H, 4-H), 4.34 (q, *J* = 6.5 Hz, 1 H, 2-H), 5.10 (br. d, *J* = 3.6 Hz, 1 H, 6-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 13.8 (q, CH_3), 24.6, 23.2 (2 q, *i*-Pr), 40.0 (t, C-5), 58.3 (q, OMe), 69.3 (d, *i*-Pr), 70.1 (d, C-2), 78.3 (d, C-4), 94.67 (d, C-6), 205.8 (s, C-3) ppm. **16** and **17**: IR (KBr): ν = 2980-2830 cm^{-1} (C-H), 1740 (C=O). MS (EI, 80 eV, 80 °C): *m*/*z* (%) = 202 ($[M]^+$, 2), 174 ($[M - CO]^+$, 3), 159 ($[M - C_3H_7]^+$, 2), 143 ($[M - C_3H_7O]^+$, 27), 130 (46), 103 (44), 87 (65), 72 (65), 59 ($[C_3H_7O]^+$, 100), 43 (81). HRMS (EI, 80 eV, 80 °C): *m*/*z* calc. for $C_{10}H_{18}O_4$: 202.1205, found: 202.1212.

Isopropyl *a*-L-cymaropyranoside (18) and **Isopropyl *b*-L-diginopyranoside (19)**



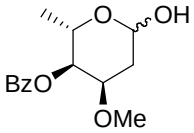
18 **19**

L-Selectride® (1.00 M in THF, 9.00 mL, 9.00 mmol) was added at -78 °C to a solution of ketones **16** and **17** (ratio 81:19, 886 mg, 4.38 mmol) in THF (12 mL). The mixture was stirred at -78 °C for 6 h. NH_4Cl-solution (sat. aq., 10 mL) was added and the mixture was warmed to r.t., then it was diluted with H_2O (20 mL). The layers were separated and the aqueous layer was extracted with EtOAc (3 × 20 mL). The combined organic layers were

dried with $MgSO_4$, filtered and concentrated. ^{1}H-NMR of the crude product mixture showed two diastereomers (*d.r.* > 95:5 each). Column chromatography (silica gel, EtOAc/hexane = 1:1) provided 732 mg of **18** (R_F ca. 0.30) as a colorless liquid and 79 mg of **19** (R_F ca. 0.20) as a colorless liquid (combined yield 91%). Due to their volatility, the products were cooled in an ice-bath when dried in vacuo.

18: $[\alpha]_D^{22}$ = –189.0 (c = 0.46, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.09, 1.17 (2 d, *J* = 6.2 Hz, 2 × 3 H, *i*-Pr), 1.22 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.70 (ddd, *J* = 3.6, 4.6, 14.7 Hz, 1 H, 2-H), 2.17 (ddd, *J* = 1.8, 3.7, 14.7 Hz, 1 H, 2-H), 2.58 (d, *J* = 9.5 Hz, 1 H, OH), 3.25 (dt, *J* = 3.6, 9.5 Hz, 1 H, 4-H), 3.38 (s, 3 H, OMe), 3.57 (dt, *J* = 3.6, 3.7 Hz, 1 H, 3-H), 3.81 (hept., *J* = 6.2 Hz, 1 H, *i*-Pr), 3.93 (dq, *J* = 6.4, 9.5 Hz, 1 H, 5-H), 4.83 (dd, *J* = 1.8, 4.6 Hz, 1 H, 1-H) ppm, in carbohydrate numbering. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 17.8 (q, CH_3), 21.5, 23.4 (2 q, *i*-Pr), 31.3 (t, C-2), 56.1 (q, OMe), 64.9 (d, C-5), 68.8 (d, *i*-Pr), 72.3 (d, C-4), 74.9 (d, C-3), 94.0 (d, C-1) ppm. **19**: $[\alpha]_D^{22}$ = –125.4 (c = 0.41, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): Line broadening of ring-proton signals occurs at room temperature. δ = 1.11, 1.16 (2 d, *J* = 6.2 Hz, 2 × 3 H, *i*-Pr), 1.27 (d, *J* = 6.6 Hz, 3 H, CH_3), 1.80-1.84 (m, 2 H, 2-H), 2.13 (br. s, 1 H, OH), 3.37 (s, 3 H, OMe), 3.60-3.65 (m, 1 H, 3-H), 3.75-3.78 (br. m, 1 H, 4-H), 3.86 (hept., *J* = 6.2 Hz, 1 H, *i*-Pr), 3.90 (br. dq, *J* = 0.7, 6.6 Hz, 1 H, 5-H), 5.00-5.02 (br. m, 1 H, 1-H) ppm. ^{13}C-NMR (126 MHz, $CDCl_3$): δ = 16.8 (q, CH_3), 21.3, 23.3 (2 q, *i*-Pr), 30.0 (t, C-2), 55.5 (q, OMe), 65.3 (d, C-5), 67.7 (d, C-4), 68.3 (d, *i*-Pr), 74.7 (d, C-3), 95.2 (d, C-1) ppm. **18**: IR (film): ν = 3470 cm^{-1} (OH), 2970-2830 (C-H). MS (FAB+): *m*/*z* (%) = 227 ($[M + Na]^+$, 7). Anal. calc. for $C_{10}H_{20}O_4$ (204.2): C 58.80, H 9.87, found: C 57.93, H 10.09 (due to the volatility of the product, repeated attempts to obtain more accurate combustion data were unsuccessful).

4-*O*-Benzoyl-L-cymaropyranose (20)



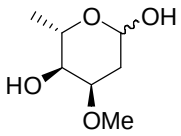
20

Alcohol **18** (56 mg, 274 μmol) was dissolved in CH_2Cl_2 (3 mL) and pyridine (1 mL). DMAP (5 mg, 45 μmol) and benzoyl chloride (70 μL, 85 mg, 603 μmol) were added at 0 °C and the mixture was stirred at r.t. for 24 h. The mixture was poured into $NaHCO_3$-solution (sat. aq., 5 mL) and washed. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 7 mL). The combined organic layers were dried with $MgSO_4$, filtered and evaporated to dryness. The crude product thus obtained was dissolved in THF (3 mL) and HCl (2 N aq., 0.20 mL) was added at r.t. After 20 h, another portion of HCl (2 N aq., 0.20 mL) was added. After 44 h, the mixture was poured into $NaHCO_3$-solution (sat. aq., 10 mL) and washed. The layers were separated and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried with $MgSO_4$, filtered and concentrated. The crude product mixture was filtered through a pad of $NaHCO_3$ absorbed on silica, with the aid of EtOAc (removal of benzoic acid). Thereafter, column chromatography (silica gel, EtOAc/hexane = 1:2 ? 1:1) provided 42 mg (58%) of **20** as a colorless, very sticky oil. ^{1}H-NMR (CD_3OD) showed an *a*/*b*-ratio of 17:83. Additionally, 15 mg of material were isolated which could be identified with *O*-benzoylated **18** (colorless oil, 18%).

$[\alpha]_D^{22} = -39.2$ (c = 0.13, H_2O, equilibrated). *a*-**20**: ^{1}H-NMR (500 MHz, CD_3OD): δ = 1.24 (d, *J* = 7.2 Hz, 3 H, CH_3), 1.98 (dt, *J* = 3.3, 14.0 Hz, 1 H, 2-H), 2.14 (ddd, *J* = 3.3, 4.5, 14.0 Hz, 1 H, 2-H), 3.42 (s, 3 H, OMe), 3.93 (dt, *J* = 3.3, 4.5 Hz, 1 H, 3-H), 4.45 (quint., *J* = 7.2 Hz, 1 H, 5-H), 4.93 (dd, *J* = 3.3, 7.2 Hz, 1 H, 4-H), 5.14 (t, *J* = 3.3 Hz, 1 H, 1-H), 7.47-7.52, 7.60-7.64, 8.05-8.08 (3 m, 5 H, Ph) ppm. ^{13}C-NMR (126 MHz, CD_3OD): δ = 17.7 (q, CH_3), 34.8 (t, C-2), 58.5 (q, OMe), 65.5 (d, C-5), 75.2 (d, C-4), 76.2 (d, C-3), 92.0 (d, C-1), 129.7, 130.7, 131.1 (3 d, Ph), 134.49 (s, Ph), 167.22 (s, CO)

ppm. *b*-**20**: ^{1}H-NMR (500 MHz, CD_3OD): δ = 1.21 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.68 (ddd, *J* = 3.2, 9.6, 13.9 Hz, 1 H, 2-H), 2.23 (ddd, *J* = 2.1, 3.2, 13.9 Hz, 1 H, 2-H), 3.40 (s, 3 H, OMe), 3.92 (dt, *J* = 3.0, 3.2 Hz, 1 H, 3-H), 4.18 (dq, *J* = 6.3, 9.8 Hz, 1 H, 5-H), 4.73 (dd, *J* = 3.0, 9.8 Hz, 1 H, 4-H), 5.09 (dd, *J* = 2.1, 9.6 Hz, 1 H, 1-H), 7.47-7.52, 7.60-7.64, 8.02-8.05 (3 m, 5 H, Ph) ppm. ^{13}C-NMR (126 MHz, CD_3OD): δ = 18.5 (q, CH_3), 37.4 (t, C-2), 58.7 (q, OMe), 69.2 (d, C-5), 76.6 (d, C-3), 77.0 (d, C-4), 93.1 (d, C-1), 129.7, 130.6, 131.1 (3 d, Ph), 134.53 (s, Ph), 167.23 (s, CO) ppm. IR (film): 3060-2830 cm^{-1} (=C-H, –C-H), 1720 (C=O), 1600, 1580 (C=C). MS (EI, 80 eV, 70 °C): *m*/*z* (%) = 266 ($[M]^+$, < 1), 190 (5), 105 ($[C_7H_5O]^+$, 100), 77 ($[C_6H_5]^+$, 36). HRMS (EI, 80 eV, 70 °C): *m*/*z* calc. for $C_{14}H_{17}O_4$, $[M - OH]^+$: 249.1127, found: 249.1125.

L-Cymarose (21)



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Acetal **18** (61 mg, 298 μmol) was dissolved in THF (2 mL) and HCl (2 N aq., 0.30 mL) was added. After 23 h at r.t., the mixture was diluted with THF (8 mL) and Dowex Marathon A2 resin (OH^--form, 520 mg) was added. After 2 h of stirring, NaOH solution (5 N aq., 0.20 mL) was added and stirring was continued for another 2 h. The mixture was further diluted with THF (5 mL) and $MgSO_4$ was directly added, followed by filtration. The filtrate was concentrated and column chromatography (silica gel, 100% EtOAc) provided the product as an oil. The oil was repeatedly taken up with Et_2O and evaporated to dryness. Prolonged drying at 0.1 mbar furnished 26 mg (54%) of **21** as colorless needles. The ^{1}H-NMR spectrum (CD_3OD) showed four species that were assigned as the two pyranose forms (*a*-pyranose: 8%, *b*-pyranose: 50%) and the two furanose forms (22% and 20%, *a*/*b*-assignment could not be made from coupling constants). Additionally, trace amounts of the free aldehyde form were detected.

m.p. 86-88 °C (Ref.:[2] 88-90 °C). $[\alpha]_D^{22}$ = –49.8 (c = 0.27, H_2O, equilibrated), Ref.:[3] – 51.5 (c = 0.33, H_2O). *a*-pyranose: ^{1}H-NMR (500 MHz, CD_3OD): δ = 1.22 (d*, 3 H, CH_3), 1.76 (ddd, *J* = 3.2, 4.0, 14.5 Hz, 1 H, 2-H), 2.17 (ddd, *J* = 2.1, 3.9, 14.5 Hz, 1 H, 2-H), 3.25 (dd, *J* = 3.2, 9.1 Hz, 1 H, 4-H), 3.47 (s, 3 H, OMe), 3.64 (dt, *J* = 3.2, 3.9 Hz, 1 H, 3-H), 4.08 (m_c, 1 H, 5-H), 5.03 (dd, *J* = 2.1, 4.0 Hz, 1 H, 1-H) ppm. ^{13}C-NMR (126 MHz, CD_3OD): δ = 18.3 (q, CH_3), 33.6 (t, C-2), 58.4 (q, OMe), 66.0 (d, C-5), 73.8 (d, C-4), 78.9 (d, C-3), 92.4 (d, C-1) ppm. *b*-pyranose: ^{1}H-NMR (500 MHz, CD_3OD): δ = 1.22 (d, *J* = 6.3 Hz, 3 H, CH_3), 1.49 (ddd, *J* = 2.6, 9.8, 14.0 Hz, 1 H, 2-H), 2.21 (ddd, *J* = 2.0, 3.4, 14.0 Hz, 1 H, 2-H), 3.15 (dd, *J* = 3.4, 9.6 Hz, 1 H, 4-H), 3.43 (s, 3 H, OMe), 3.59 (dt, *J* = 2.6, 3.4 Hz, 1 H, 3-H), 3.74 (dq, *J* = 6.3, 9.6 Hz, 1 H, 5-H), 4.94 (dd, *J* = 2.0, 9.8 Hz, 1 H, 1-H) ppm. ^{13}C-NMR (126 MHz, CD_3OD): δ = 18.7 (q, CH_3), 36.7 (t, C-2), 58.0 (q, OMe), 71.4 (d, C-5), 74.5 (d, C-4), 79.2 (d, C-3), 92.9 (d, C-1) ppm. Minor furanose: ^{1}H-NMR (500 MHz, CD_3OD): δ = 1.18 (d, *J* = 6.4 Hz, 3 H, CH_3), 1.95 (dt, *J* = 1.4, 15.2 Hz, 1 H, 2-H), 2.11 (ddd, *J* = 5.4, 6.7, 15.2 Hz, 1 H, 2-H), 3.32 (s, 3 H, OMe), 3.67-3.70 (m, 1 H, 5-H), 3.91-3.94 (m, containing 3-H, 4-H), 5.45 (dd, *J* = 1.4, 5.4 Hz, 1 H, 1-H) ppm. ^{13}C-NMR (126 MHz, CD_3OD): δ = 19.3 (q, CH_3), 40.0 (t, C-2), 57.1 (q, OMe), 68.5 (d, C-5), 82.1 (d, C-3), 88.9 (d, C-4), 99.6 (d, C-1) ppm. Major furanose: ^{1}H-NMR (500 MHz, CD_3OD): δ = 1.21 (d, *J* = 6.3 Hz, 3 H, CH_3), 2.04 (ddd, *J* = 3.8, 6.6, 13.6 Hz, 1 H, 2-H), 2.09 (ddd, *J* = 3.9, 5.3, 13.6 Hz, 1 H, 2-H), 3.30 (s, 3 H, OMe), 3.71-3.78 (m, containing 4-H, 5-H), 4.05-4.09 (m, 1 H, 3-H), 5.49 (dd, *J* = 3.8, 5.3 Hz, 1 H, 1-H) ppm. ^{13}C-NMR (126 MHz, CD_3OD): δ = 19.5 (q, CH_3), 41.0 (t, C-2), 56.9 (q, OMe), 69.2 (d, C-5), 82.4 (d, C-3), 89.4 (d, C-4), 99.8 (d, C-1) ppm. (*): Coupling constant could not be determined. The spectroscopic data are in agreement with Ref.[4]

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