Proline Organocatalysis as a New Tool for the Asymmetric Synthesis of Ulosonic Acid Precursors

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14c': To a stirred solution of aldol product (S,R)-8c (248 mg, 1 mmol) in dry MeOH (10 mL) Amberlyst®-15 (496 mg) was added. After complete conversion (monitored by TLC, ~ 4 h) the acid ion-exchange resin was removed by filtration and the solvent was evaporated under vacuum. The hemiketal 14c' was purified by flash chromatography (ethyl acetate/methanol, 65:5) affording a colourless sticky oil as mixture of α and β furanose rings (185 mg, 89%). [α]D 24 +23.4 (c 0.97 in MeOH); Found C, 46.3, H 7.4. Calc, for C18H36O6: C, 46.1, H, 7.7; IR (CHCl3) νmax/cm−1 3422, 2938, 2837, 1646, 1454, 1195, 1086, 755; 1H NMR δΗ (400 MHz, CD3OD) 1.76 (dd, 1H, CHH, J 5.4 Hz, J 13.7 Hz), 2.10 (dd, 1H, CHH, J 7.8 Hz, J 13.6 Hz), 2.18 (dd, 1H, CHH, J 8.4 Hz, J 13.6 Hz), 2.43 (dd, 1H, CHH, J 8.0 Hz, J 13.7 Hz), 3.4-3.7 (m, 11H, CH2OH, CH2OH, CH2OH, CH2OH, CH2OH), 3.41 (s, 3H, OCH3), 3.42 (s, 3H, OCH3), 3.47 (s, 3H, OCH3), 3.51 (s, 3H, OCH3), 3.91 (dt, 1H, CH2OH, J 3.6 Hz, J 5.4 Hz), 4.02 (dt, 1H, CHOH, J 5.4 Hz, J 8.0 Hz), 4.16 (pseudo q, 1H, CHOH, J 8.1 Hz), 4.25 (s, 1H, CH(OCH3)2); 13C NMR δC (125 MHz; CD3OD) 39.1 (CH3C), 40.3 (CH3C), 56.6 (2 x CH3), 58.3 (CH3), 58.5 (CH3), 63.6 (CH2OH), 63.7 (CH2OH), 71.4 (CH2CHOH), 72.7 (CH2CHOH), 87.7 (CH2CHO), 88.0 (CH2CHO), 106.0 (CH(OCH3)2), 106.9 (CH(OCH3)2), 109.6 (C), 110.2 (C). m/z (ESI): 209 (M+1, 4), 191 (M−17, 24), 176 (M−32, 100), 158 (M−50, 40) 148 (M−60, 55).
**14c**: To a stirred solution of aldol product (R,R)-8c (124 mg, 0.5 mmol) in dry MeOH (5 mL) Amberlyst®-15 (248 mg) was added. After complete conversion (monitored by TLC, ~3.5 h) the acid ion-exchange resin was removed by filtration and the solvent was evaporated under vacuum. The hemiketal 14c was purified by flash chromatography (ethyl acetate/ methanol, 95:5) affording a colourless sticky oil as a single pyranose form (90 mg, 87%). [α]D24 -10.8 (c 1.01 in MeOH); Found C, 46.5, H 8.1. Calc, for C8H16O6: C, 46.1, H, 7.7; 1H NMR δH (400 MHz, CD3OD+D2O) 1.61 (dd, 1H, CHH, J11.6 Hz, J13.1 Hz), 1.92 (dd, 1H, CCHH, J5.3 Hz, J13.1 Hz), 3.23-3.52 (m, 5H, OCH2, OCH2CHO, CCH2CHOH, COH), 3.45 (s, 3H, OCH3), 3.48 (s, 3H, OCH3), 3.62-3.70 (m, 2H, OCH2CHOH, CCH2CHOH), 4.25 (s, 1H, CH(OCH2)2); 13C NMR δC (125 MHz; CD3OD+D2O) 35.8 (CH2C), 56.8 (OCH2), 58.4 (OCH3), 64.6 (CHOH), 72.5 (CHOH), 102.4 (COH), 105.8 (CH(OCH2)2); m/z (EI): 208 (M+, 0.1), 191 (M+17, 2), 158 (M+50, 18), 147 (M+61, 100), 96 (M+112, 43).