

Supplementary Materials

Evolution of Enzymatic Activities in the Enolase Superfamily:

L-Fuconate Dehydratase from *Xanthomonas campestris* †

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The following hexonic acids, pentonic acids and tetronic acids were prepared from the corresponding hexoses, pentoses and tetroses by bromine oxidation: D-allonate, L-allonate, D-altronate, L-altronate, L-gluconate, D-idonate, L-idonate, D-talonate, L-talonate, D-fuconate, L-fuconate, L-rhamnonate, D-ribonate, L-ribonate, D-arabinonate, L-arabinonate, L-xylonate, L-lyxonate, D-threonate. D-Gluconate, D-xylonate and L-threonate were purchased from Sigma Aldrich.

Synthesis of L-fuconate. The synthesis of L-fuconate is described as a general procedure. In a 500 mL flask, L-fucose (5 g, 30 mmol) was oxidized with bromine (1.85 mL, 36 mmol) in the presence of barium benzoate (18 g, 42 mmol) in a 250 mL reaction volume. The mixture was kept in the dark for 36 hrs, and excess bromine was removed by aeration. Ionic barium was removed with the addition of sulfuric acid (42 mmol), and the mixture was filtered to remove barium sulfate. The mixture was filtered through a layer of decolorizing carbon (3 g), and residual benzoate was removed from the colorless filtrate by 3 extractions with chloroform (100 mL). Residual hydrobromic acid was removed by stirring with silver carbonate (9.9 g, 36 mmol). After filtration, the solution was rotary evaporated to approximately 50 mL. The pH of the filtrate was adjusted to

10.0 by addition of ammonium hydroxide, and L-fuconate was purified by anion-exchange chromatography. L-Fuconate was purified by elution from a column of Dowex AG 1X8 (formate form) using a linear gradient (2.3 L) of 0 M to 1.5 M formic acid. Fractions containing L-fuconate were pooled and formic acid was removed by evaporation to yield L-fucono-lactone. L-Fuconate was obtained from the lactone by base hydrolysis. L-Fucono-lactone was dissolved in solution, and a solution of NaOH (5 M) was added to increase the pH to 10-12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of L-fuconate.

^1H NMR (500 MHz, D_2O). δ 4.08 (d, J = 1.57 Hz, 1H, C2), 3.92 (qd, J = 1.88 and 6.6 Hz, 1H, C5), 3.75 (dd, J = 1.56 and 9.46 Hz, 1H, C3), 3.27 (dd, J = 1.85 and 9.47 Hz, 1H, C4), 1.07 (d, J = 6.63 Hz, 3H, C6).

Synthesis of D-allonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.05 (d, J = 3.2 Hz, 1H, C2), 3.89 (dd, J = 3.1 and 6.9 Hz, 1H, C3), 3.76-3.73 (m, 1H, C5), 3.70-3.67 (m, 1H, C4), 3.69-3.67 (m, 1H, C6), 3.53 (dd, J = 7.05 and 11.91 Hz, 1H, C6).

Synthesis of L-allonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.05 (d, J = 3.2 Hz, 1H, C2), 3.89 (dd, J = 3.1 and 6.9 Hz, 1H, C3), 3.76-3.73 (m, 1H, C5), 3.70-3.67 (m, 1H, C4), 3.69-3.67 (m, 1H, C6), 3.53 (dd, J = 7.05 and 11.91 Hz, 1H, C6).

Synthesis of D-altronate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.10 (d, $J = 1.66$ Hz, 1H, C2), 3.82 (dd, $J = 1.65$ and 8.88 Hz, 1H, C3), 3.80 (m, 1H, C5), 3.68 (dd, $J = 3.02$ and 11.89 Hz, 1H, C6), 3.64 (dd, $J = 4.58$ and 8.87 Hz, 1H, C4), 3.56 (dd, $J = 7.59$ and 11.87 Hz, 1H, C6).

Synthesis of L-altronate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.10 (d, $J = 1.66$ Hz, 1H, C2), 3.82 (dd, $J = 1.65$ and 8.88 Hz, 1H, C3), 3.80 (m, 1H, C5), 3.68 (dd, $J = 3.02$ and 11.89 Hz, 1H, C6), 3.64 (dd, $J = 4.58$ and 8.87 Hz, 1H, C4), 3.56 (dd, $J = 7.59$ and 11.87 Hz, 1H, C6).

Synthesis of L-gluconate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 3.95 (d, $J = 3.75$ Hz, 1H, C2), 3.85 (dd, $J = 3.25$ and 3.72 Hz, 1H, C3), 3.65 (dd, $J = 2.57$ and 11.7 Hz, 1H, C6), 3.60-3.58 (m, 2H, C4 and C5), 3.49 (dd, $J = 6.56$ and 11.74 Hz, 1H, C6).

Preparation of D-mannonate. D-Mannono- γ -lactone was purchased from TCI and dissolved in solution. A solution of NaOH (5 M) was added to increase the pH to 10-12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of D-mannonate.

^1H NMR (500 MHz, D_2O). δ 3.95 (d, $J = 5.71$ Hz, 1H, C2), 3.83 (dd, $J = 0.91$ and 5.78 Hz, 1H, C3), 3.66 (dd, $J = 2.22$ and 11.74 Hz, 1H, C6), 3.57-3.55 (m, 2H, C4 and C5), 3.47 (dd, $J = 6.3$ and 11.79 Hz, 1H, C6).

Preparation of L-mannonate. L-Mannono- γ -lactone was purchased from Aldrich and dissolved in solution. A solution of NaOH (5 M) was added to increase the pH to 10-

12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of L-mannonate.

^1H NMR (500 MHz, D_2O). δ 3.95 (d, $J = 5.71$ Hz, 1H, C2), 3.83 (dd, $J = 0.91$ and 5.78 Hz, 1H, C3), 3.66 (dd, $J = 2.22$ and 11.74 Hz, 1H, C6), 3.57–3.55 (m, 2H, C4 and C5), 3.47 (dd, $J = 6.3$ and 11.79 Hz, 1H, C6).

Preparation of D-gulonate. D-Gulono- γ -lactone was purchased from Sigma and dissolved in solution. A solution of NaOH (5 M) was added to increase the pH to 10-12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of D-gulonate.

^1H NMR (500 MHz, D_2O). δ 3.96 (d, $J = 5.3$ Hz, 1H, C2), 3.71 (dd, $J = 2.98$ and 5.35 Hz, 1H, C3), 3.69-3.64 (m, 2H, C4 and C5), 3.56 (dd, $J = 3.8$ and 11.85 Hz, 1H, C6), 3.46 (dd, $J = 6.6$ and 11.87 Hz, 1H, C6).

Preparation of L-gulonate. L-Gulono- γ -lactone was purchased from Sigma and dissolved in solution. A solution of NaOH (5 M) was added to increase the pH to 10-12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of L-gulonate.

^1H NMR (500 MHz, D_2O). δ 3.96 (d, $J = 5.3$ Hz, 1H, C2), 3.71 (dd, $J = 2.98$ and 5.35 Hz, 1H, C3), 3.69-3.64 (m, 2H, C4 and C5), 3.56 (dd, $J = 3.8$ and 11.85 Hz, 1H, C6), 3.46 (dd, $J = 6.6$ and 11.87 Hz, 1H, C6).

Synthesis of D-idonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 3.97 (d, $J = 2.44$ Hz, 1H, C2), 3.85 (dd, $J = 2.4$ and 7.03 Hz, 1H, C3), 3.70 (m, 1H, C5), 3.58 (dd, $J = 2.7$ and 7.07 Hz, 1H, C4), 3.56-3.49 (m, 2H, C6).

Synthesis of L-idonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 3.97 (d, $J = 2.44$ Hz, 1H, C2), 3.85 (dd, $J = 2.4$ and 7.03 Hz, 1H, C3), 3.70 (m, 1H, C5), 3.58 (dd, $J = 2.7$ and 7.07 Hz, 1H, C4), 3.56-3.49 (m, 2H, C6).

Preparation of D-galactonate. D-Galactono- γ -lactone was purchased from Sigma and dissolved in solution. A solution of NaOH (5 M) was added to increase the pH to 10-12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of D-galactonate.

^1H NMR (500 MHz, D_2O). δ 4.12 (d, $J = 1.53$ Hz, 1H, C2), 3.82-3.81 (m, 1H, C5), 3.80 (dd, $J = 1.58$ and 9.58 Hz, 1H, C3), 3.54 (m, 1H, C4), 3.53 (dd, $J = 1.13$ and 9.70 Hz, 1H, C6), 3.47 (dd, $J = 1.41$ and 9.68 Hz, 1H, C6).

Preparation of L-galactonate. L-Galactono- γ -lactone was purchased from Sigma and dissolved in solution. A solution of NaOH (5 M) was added to increase the pH to 10-12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of L-galactonate.

^1H NMR (500 MHz, D_2O). δ 4.12 (d, $J = 1.53$ Hz, 1H, C2), 3.82-3.81 (m, 1H, C5), 3.80 (dd, $J = 1.58$ and 9.58 Hz, 1H, C3), 3.54 (m, 1H, C4), 3.53 (dd, $J = 1.13$ and 9.70 Hz, 1H, C6), 3.47 (dd, $J = 1.41$ and 9.68 Hz, 1H, C6).

Synthesis of D-talonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.07 (d, $J = 2.94$ Hz, 1H, C2), 3.86 (dd, $J = 2.95$ and 8.61 Hz, 1H, C3), 3.80 (m, 1H, C5), 3.64 (dd, $J = 1.89$ and 8.6 Hz, 1H, C4), 3.53 (m, 2H, C6).

Synthesis of L-talonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.07 (d, $J = 2.94$ Hz, 1H, C2), 3.86 (dd, $J = 2.95$ and 8.61 Hz, 1H, C3), 3.80 (m, 1H, C5), 3.64 (dd, $J = 1.89$ and 8.6 Hz, 1H, C4), 3.53 (m, 2H, C6).

Synthesis of D-fuconate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.08 (d, $J = 1.57$ Hz, 1H, C2), 3.92 (qd, $J = 1.88$ and 6.6 Hz, 1H, C5), 3.75 (dd, $J = 1.56$ and 9.46 Hz, 1H, C3), 3.27 (dd, $J = 1.85$ and 9.47 Hz, 1H, C4), 1.07 (d, $J = 6.63$ Hz, 3H, C6).

Synthesis of L-rhamnonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 3.97 (d, $J = 5.13$ Hz, 1H, C2), 3.83 (dd, $J = 2.17$ and 5.15 Hz, 1H, C3), 3.69 (m, 1H, C5), 3.41 (dd, $J = 2.18$ and 7.2 Hz, 1H, C4), 1.07 (d, $J = 6.38$ Hz, 3H, C6).

Synthesis of D-ribonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.01 (d, J = 3.49 Hz, 1H, C2), 3.75 (dd, J = 3.50 and 3.42 Hz, 1H, C3), 3.68 (td, J = 3.17, 2.35 and 10.34 Hz, 1H, C4), 3.50 (m, 2H, C5).

Synthesis of L-ribonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.01 (d, J = 3.49 Hz, 1H, C2), 3.75 (dd, J = 3.50 and 3.42 Hz, 1H, C3), 3.68 (td, J = 3.17, 2.35 and 10.34 Hz, 1H, C4), 3.50 (m, 2H, C5).

Synthesis of D-arabinonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.09 (d, J = 1.73 Hz, 1H, C2), 3.70 (dd, J = 2.70 and 10.60 Hz, 1H, C3), 3.60 (m, 2H, C5), 3.58 (td, J = 2.70, 2.73 and 7.75 Hz, 1H, C4).

Synthesis of L-arabinonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.09 (d, J = 1.65 Hz, 1H, C2), 3.72 (dd, J = 2.64 and 3.38 Hz, 1H, C3), 3.60 (m, 2H, C5), 3.59 (td, J = 2.67 and 7.84 Hz, 1H, C4).

Synthesis of L-xylonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 3.92 (d, J = 2.59 Hz, 1H, C2), 3.73 (dd, J = 2.61 and 3.17 Hz, 1H, C3), 3.67 (td, J = 3.78 and 6.50 Hz, 1H, C4), 3.55 (m, 2H, C5).

Preparation of D-lyxonate D-Lyxono- γ -lactone was purchased from TCI and dissolved in solution. A solution of NaOH (5 M) was added to increase the pH to 10-12; after 48 hrs the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of D-lyxonate.

^1H NMR (500 MHz, D_2O). δ 4.00 (d, $J = 5.14$ Hz, 1H, C2), 3.77 (td, $J = 2.89$ and 6.09 Hz, 1H, C4), 3.68 (dd, $J = 2.88$ and 2.56 Hz, 1H, C3), 3.53 (m, 2H, C5).

Synthesis of L-lyxonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 4.00 (d, $J = 5.14$ Hz, 1H, C2), 3.76 (td, $J = 2.80$ and 4.93 Hz, 1H, C4), 3.68 (dd, $J = 1.41$ and 2.65 Hz, 1H, C3), 3.52 (m, 2H, C5).

Preparation of D-erythronate. D-Erythrono- γ -lactone was purchased from Aldrich and dissolved in solution. A solution of NaOH (5 M) was added to increase the pH to 10-12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of D-erythronate.

^1H NMR (500 MHz, D_2O). δ 3.93 (d, $J = 4.02$ Hz, 1H, C2), 3.79 (m, 1H, C3), 3.49 (d, $J = 1.78$ Hz, 1H, C4), 3.47 (d, $J = 0$ Hz, 1H, C4).

Synthesis of D-threonate. The reaction procedure was the same as described for the synthesis of L-fuconate. The yield was 40%.

^1H NMR (500 MHz, D_2O). δ 3.84 (d, $J = 2.55$ Hz, 1H, C2), 3.81 (m, 1H, C3), 3.53 (dd, $J = 5.14$ and 11.5 Hz, 1H, C4), 3.46 (dd, $J = 7.73$ and 11.5 Hz, 1H, C4).

The following hexaric acids and pentaric acids were prepared from the corresponding hexoses and pentitols either by 4-acetamido-TEMPO oxidation of the aldose or by nitric acid oxidation of the aldose or alditol: *meso*-allarate, D-talarate, L-talarate, L-glucarate, D-mannarate, L-mannarate, D-idarate, L-idarate, *meso*-ribarate, D-arabinarate, L-arabinarate, *meso*-xyllarate. D-Glucarate, *meso*-galactarate, D-tartrate, L-tartrate, and *meso*-tartrate were purchased from Sigma, and the aldoses were purchased from Omicron.

Synthesis of meso-Allarate. The synthesis of *meso*-allarate using 4-acetamido-TEMPO oxidation is described as a general procedure. In a 300 mL flask, D-allose (2.03 g, 11.7 mmol), 4-acetamido-TEMPO (0.025 g, 0.133 mmol) and sodium bromide (0.264g, 2.56 mmol) were dissolved in ddH₂O in a 50 mL reaction volume at 0 °C. The reaction mixture was maintained at pH 11.5 with NaOH, and chilled hypochlorous acid (Clorox Industrial bleach) solution (65.7 mL of 6.15 % (v/v), 50 mmol) was added dropwise to the mixture over 44 min. The rate of hypochlorous acid addition was controlled to maintain the temperature of the reaction mixture below 4.7 °C, and the pH of the mixture was maintained between 10.3 and 12.0 with NaOH. The oxidation was complete after 2 hrs, and the reaction mixture was concentrated under rotary evaporation to approximately 30 mL. *meso*-Allarate was precipitated from the mixture with the addition of 100 mL of chilled absolute ethanol, and the white precipitate was dissolved in 30 mL of ddH₂O. The process of precipitation with ethanol was repeated, and the white precipitate of *meso*-allarate was lyophilized. The lyophilized *meso*-allarate was dissolved in a minimal volume of ddH₂O, and the pH of the solution was adjusted to 10 with KOH. After 10 hrs, the reaction volume was adjusted to 50 mL, and *meso*-allarate was purified by anion-exchange chromatography. *meso*-Allarate was purified by elution from a column of Dowex AG 1X8 (formate form) using a linear gradient (2.3 L) of 0 M to 2 M formic acid. Fractions containing *meso*-allarate were pooled and formic acid was removed by evaporation to yield *meso*-allaro-lactone. *meso*-Allarate was obtained from the lactone by base hydrolysis. *meso*-Allaro-lactone was dissolved in solution, and a solution of KOH (3 M) was added to increase the pH to 10-12; after 1 hr the reaction was

stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of *meso*-allarate. The yield was 65%.

^1H NMR (500 MHz, D_2O). δ 4.06 (t, $J = 1.53$ and 73.4 Hz, 2H, C2 and C5), 3.90 (t, $J = 1.53$ and 73.4 Hz, 2H, C3 and C4).

Synthesis of D-talarate. The reaction procedure was the same as described for the synthesis of *m*-allarate. The yield was 65%.

^1H NMR (500 MHz, D_2O). δ 4.05 (d, $J = 1.61$ Hz, 1H, C5), 4.01 (d, $J = 3.25$ Hz, 1H, C2), 3.88 (dd, $J = 1.56$ and 8.96 Hz, 1H, C4), 3.77 (dd, $J = 1.56$ and 8.96 Hz, 1H, C3).

Synthesis of L-talarate. The reaction procedure was the same as described for the synthesis of *m*-allarate. The yield was 65%.

^1H NMR (500 MHz, D_2O). δ 4.05 (d, $J = 1.61$ Hz, 1H, C5), 4.01 (d, $J = 3.25$ Hz, 1H, C2), 3.88 (dd, $J = 1.56$ and 8.96 Hz, 1H, C4), 3.77 (dd, $J = 1.56$ and 8.96 Hz, 1H, C3).

Synthesis of L-glucarate. The reaction procedure was the same as described for the synthesis of *m*-allarate. The yield was 65%.

^1H NMR (500 MHz, D_2O). δ 4.14 (m, $J = 2.36$ and 4.47 Hz, 2H, C2 and C5), 4.05 (qd, $J = 2.62$ and 7.39 Hz, 1H, C4), 3.94 (td, $J = 4.4$ and 9.15 , 1H, C5).

Synthesis of D-mannarate. The reaction procedure was the same as described for the synthesis of *m*-allarate. The yield was 65%.

^1H NMR (500 MHz, D_2O). δ 3.79 (dd, $J = 0.49$ and 5.8 Hz, 2H, C2 and C5), 3.95 (dd, $J = 0.49$ and 5.8 Hz, 2H, C3 and C4).

Synthesis of L-mannarate. The reaction procedure was the same as described for the synthesis of *m*-allarate. The yield was 65%.

^1H NMR (500 MHz, D_2O). δ 3.79 (dd, $J = 0.49$ and 5.8 Hz, 2H, C2 and C5), 3.95 (dd, $J=0.49$ and 5.8 Hz, 2H, C3 and C4).

Synthesis of D-Idarate. The synthesis of D-idarate using nitric acid oxidation is described as a general procedure. In a 100 mL flask, D-idose (3.0 g, 20 mmol) was oxidized with 10 mL of nitric acid (15.8 N) in the presence of sodium nitrite (0.14 g, 0.0002 mmol) and refluxed for 10 hrs. 100 mL of ddH₂O was added to the reaction, and the mixture was further refluxed for 5 hrs. The mixture was lyophilized, and the resulting residue was dissolved in a minimal volume of ddH₂O, and the pH of the mixture was adjusted to 10 with KOH. After 5 hrs, the reaction volume was adjusted to 100 mL and the mixture was filtered through a layer of decolorizing carbon (5 g), and D-idarate was purified by anion-exchange chromatography. D-Idarate was purified by elution from a column of Dowex AG 1X8 (formate form) using a linear gradient (2.3 L) of 0 M to 2 M formic acid. Fractions containing D-idarate were pooled and formic acid was removed by evaporation to yield D-idaro-lactone. D-Idarate was obtained from the lactone by base hydrolysis. D-Idaro-lactone was dissolved in solution, a solution of KOH (3 M) was added to increase the pH to 10-12; after 1 hr the reaction was stopped by lowering the pH to 8.0 with 1 M HCl to obtain a stock solution of D-idarate. The yield was 60%.

^1H NMR (500 MHz, D_2O). δ 4.00 (t, $J = 0.91$ and 68.9 Hz, 2H, C2 and C5), 3.86 (t, $J = 0.91$ and 68.9 Hz, 2H, C3 and C4).

Synthesis of L-idarate. The reaction procedure was the same as described for the synthesis of D-idarate. The yield was 60%.

^1H NMR (500 MHz, D_2O). δ 4.00 (t, $J = 0.91$ and 68.9 Hz, 2H, C2 and C5), 3.86 (t, $J = 0.91$ and 68.9 Hz, 2H, C3 and C4).

Synthesis of meso-ribarate. The reaction procedure was the same as described for the synthesis of D-idarate, using D-ribitol. The yield was 60%.

^1H NMR (500 MHz, D_2O). δ 3.89 (m, $J = 5.4$ Hz, 3H, C2, C3 and C4).

Synthesis of D-arabinarate. The reaction procedure was the same as described for the synthesis of D-idarate, using D-arabinitol. The yield was 60%.

^1H NMR (500 MHz, D_2O). δ 4.04 (d, $J = 1.5$ Hz, 1H, C4), 3.91 (d, $J = 7.21$ Hz, 1H, C2), 3.88 (dd, $J = 1.49$ and 7.21 Hz, 1H, C3).

Synthesis of L-arabinarate. The reaction procedure was the same as described for the synthesis of D-idarate, using L-arabinitol. The yield was 60%.

^1H NMR (500 MHz, D_2O). δ 4.04 (d, $J = 1.5$ Hz, 1H, C4), 3.91 (d, $J = 7.21$ Hz, 1H, C2), 3.88 (dd, $J = 1.49$ and 7.21 Hz, 1H, C3).

Synthesis of meso-xylarate. The reaction procedure was the same as described for the synthesis of D-idarate, using *meso*-xylitol. The yield was 60%.

^1H NMR (500 MHz, D_2O). δ 3.99 (d, $J = 3.72$ Hz, 1H, C3), 3.95 (d, $J = 3.92$ Hz, 1H, C2), 3.93 (d, $J = 2.44$ Hz, 1H, C4).