Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.


*Electronic Supplementary Information (ESI)*

# Structure-Selectivity Relationships for Polyol Hydrogenolysis over Ru Catalysts

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**GC data for identification of 6-deoxy hexitols and pentitols is shown in Figures S-1 and S-2.**

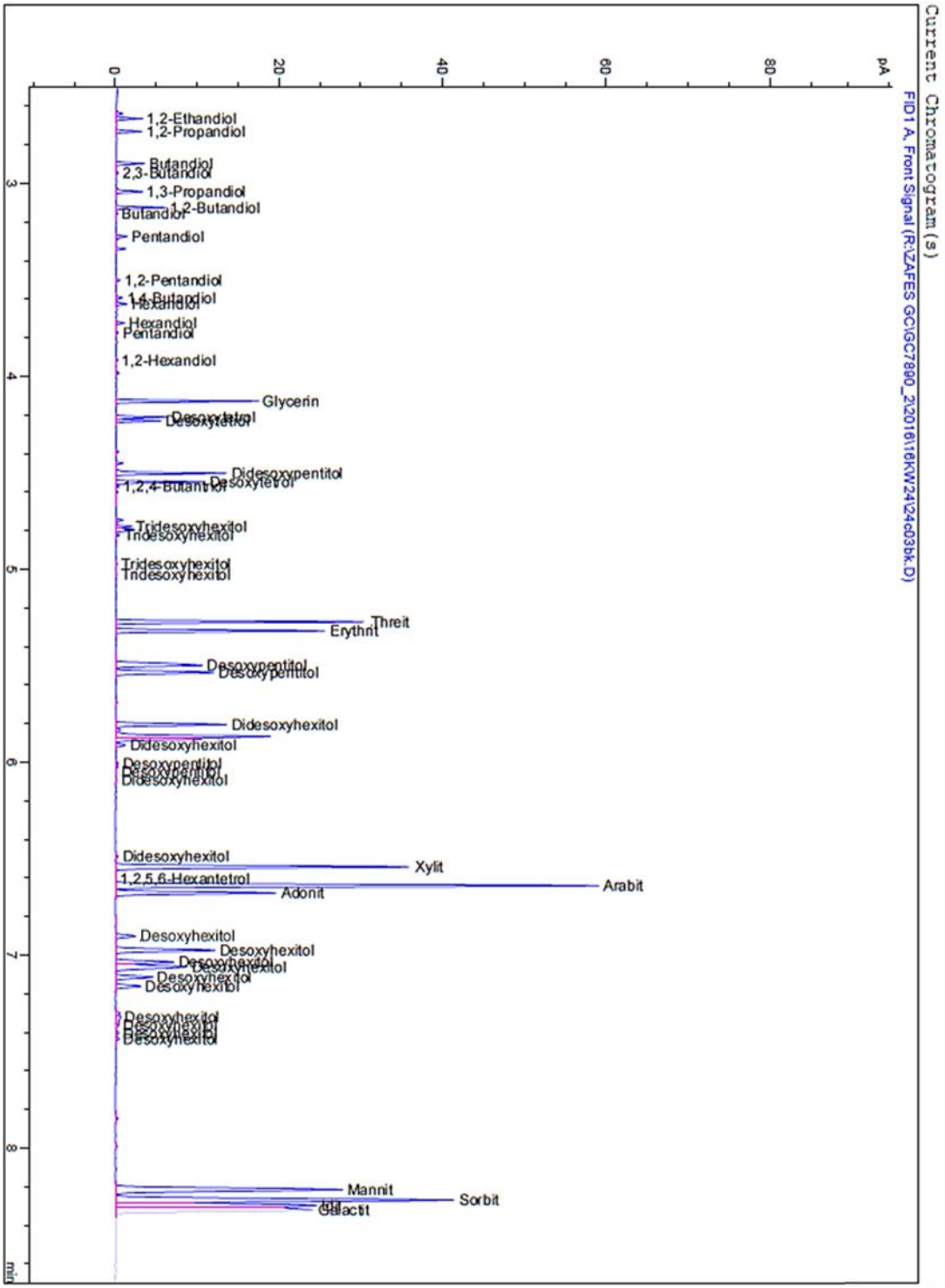



**Figure S-1:** GC chromatogram of the product mixture obtained from mannitol hydrogenolysis (aqueous 7.5 wt-% mannitol solution) over $Ru/Al_2O_3$ at 180 °C, 150 bar $H_2$ and 5 h reaction time. The main products are C5 polyols (xylitol, arabitol, as well as ribitol (labeled as Adonit)) at 6.6 min retention time. At about 7.0 to 7.2 min several 6-deoxy hexitols stereoisomers are detected.

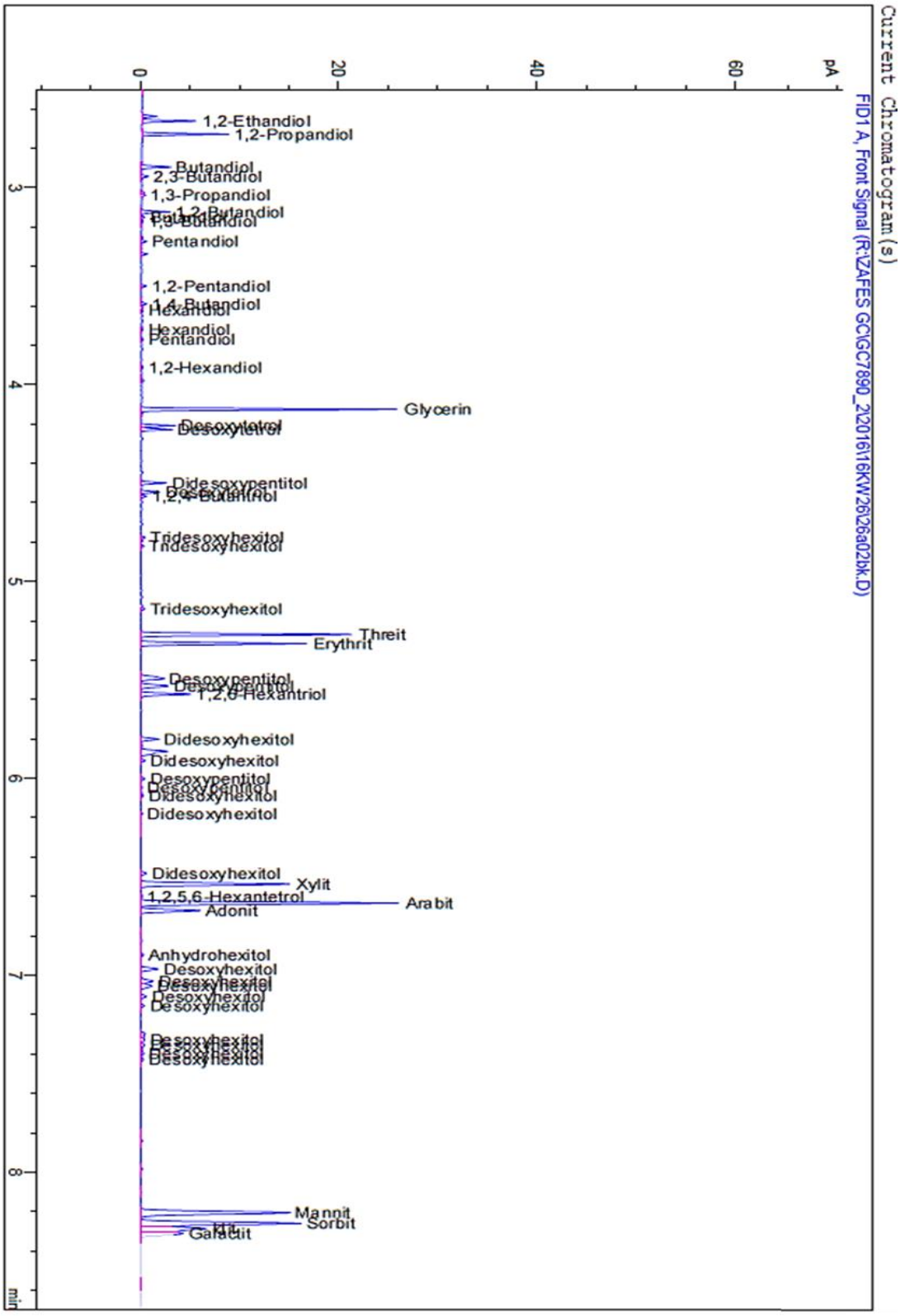



**Figure S-2:** GC chromatogram of the product mixture obtained from mannitol hydrogenolysis (aqueous 7.5 wt-% mannitol solution) over $Ru/Al_2O_3$ at 220 °C, 150 bar $H_2$ and 5 h reaction time. The main products are gaseous C1 polyols and only 13 mol-% of the applied carbon is left in the liquid phase. The liquid phase composition mainly accounts for C5 polyols (xylitol, arabitol, and ribitol (labeled as Adonit)) at 6.6 min retention time, the C4 polyols erythritol and threitol (5.3 min), and the C3 polyol glycerol (3.1 min).

**GC data for identification of 6-deoxy hexitols and 1,6-dideoxy hexitols is shown in Figures S-3 to S-7 (see also DOI: 10.1039/C7CY02426F).**

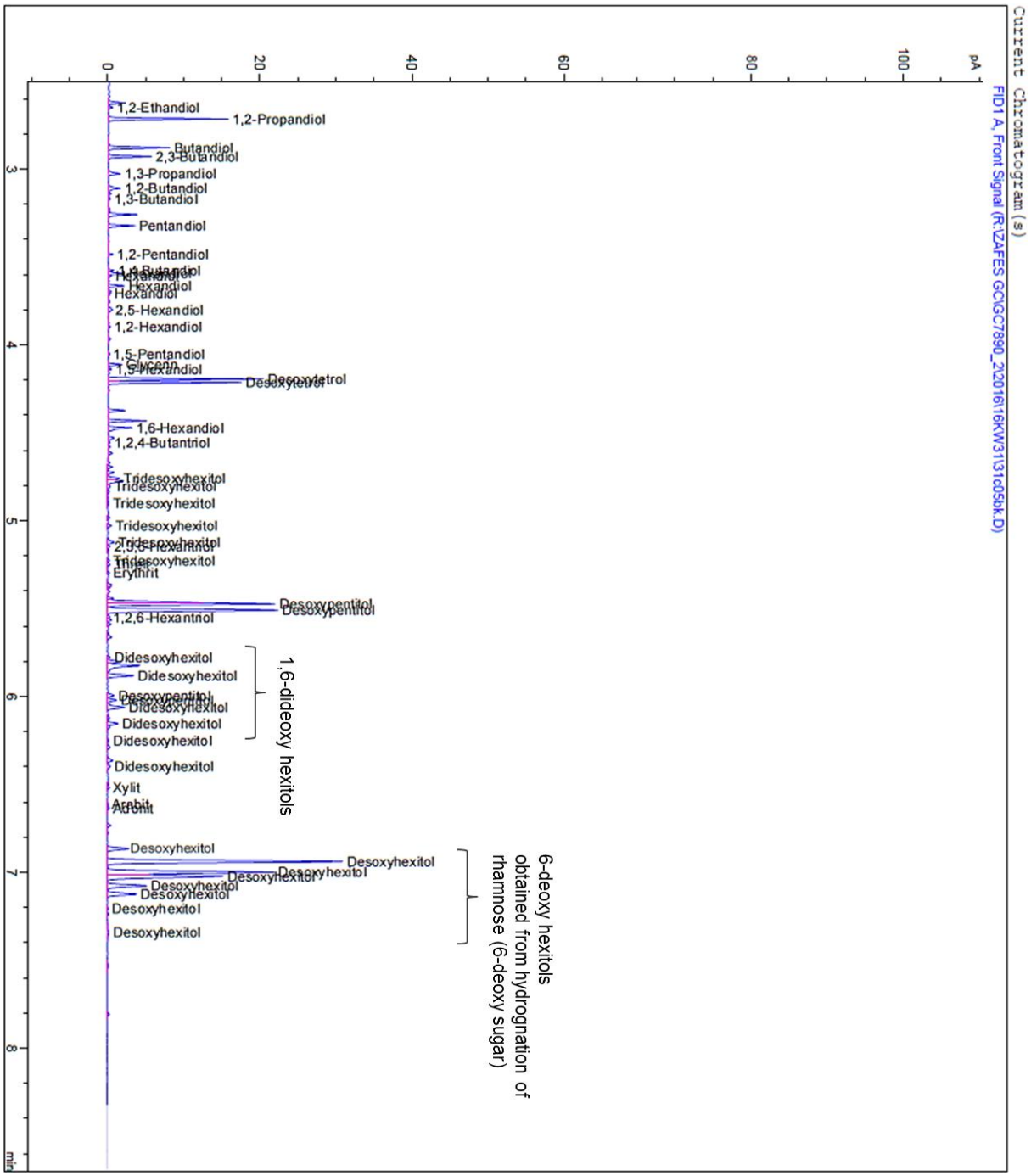



**Figure S-3:** GC chromatogram of the product mixture obtained from rhamnose (6-deoxy sugar) hydrogenolysis (aqueous 7.5 wt-% rhamnose solution) over $Ru/Al_2O_3$ at 180 °C, 150 bar $H_2$ and 2.5 h reaction time. 6-deoxy hexitols (multiple stereoisomers) obtained from rhamnose hydrogenation are detected at 7.0 to 7.2 min retention time. 1,6-dideoxy hexitol (multiple stereoisomers) are detected at 5.8 to 6.2 min retention time and deoxy pentitols (two stereoisomers) at 5.5 min retention time. It can be excluded dideoxy hexitos at 5.8 to 6.2 min retention time are different constitutional isomers because other dideoxy hexitols (3,6-dideoxy and 3,4-dideoxy hexitols) were identified by NMR analysis and are detected at other retention times as shown in Figure S-5.

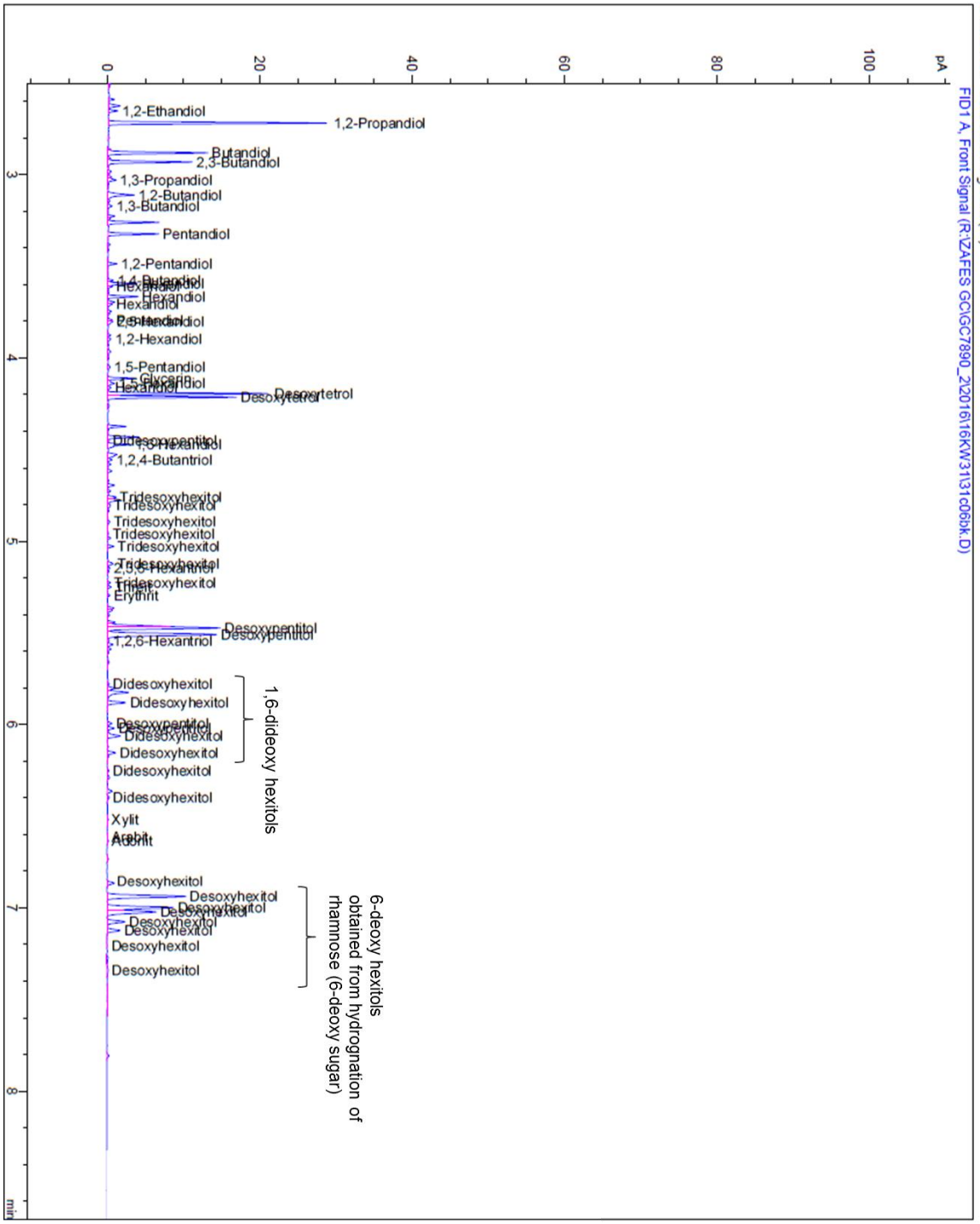



**Figure S-4:** GC chromatogram of the product mixture obtained from rhamnose (6-deoxy sugar) hydrogenolysis (aqueous 7.5 wt-% rhamnose solution) over $Ru/Al_2O_3$ at 180 °C, 150 bar $H_2$ and 5 h reaction time. 6-deoxy hexitols (multiple stereoisomers) obtained from rhamnose hydrogenation are detected at 7.0 to 7.2 min retention time. 1,6-dideoxy hexitol (multiple stereoisomers) are detected at 5.8 to 6.2 min retention time and deoxy pentitols (two stereoisomers) at 5.5 min retention time.

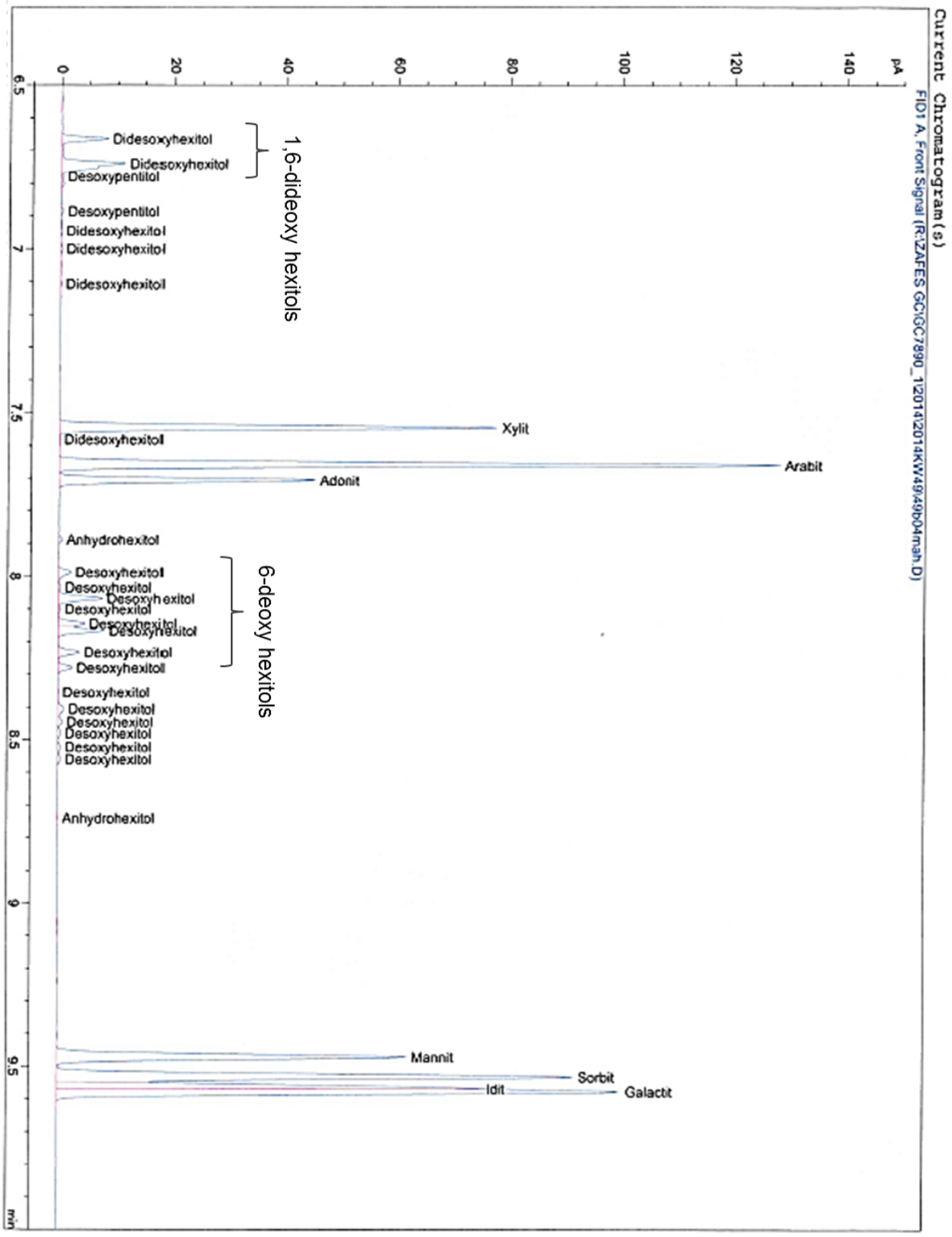



**Figure S-5:** GC chromatogram of the product mixture obtained from mannitol hydrogenolysis (aqueous 7.5 wt-% mannitol solution) over $Ru/Al_2O_3$ at 160 °C, 150 bar $H_2$ and 5 h reaction time. Six stereoisomers of 6-deoxy hexitols (1,2,3,4,5-hexanepentols) are detected at 8.0 to 8.3 min. 1,6-dideoxy hexitols are detected at 6.6 to 6.8 min retention time. The corresponding GC-MS analysis is shown in **Figure S-6**.

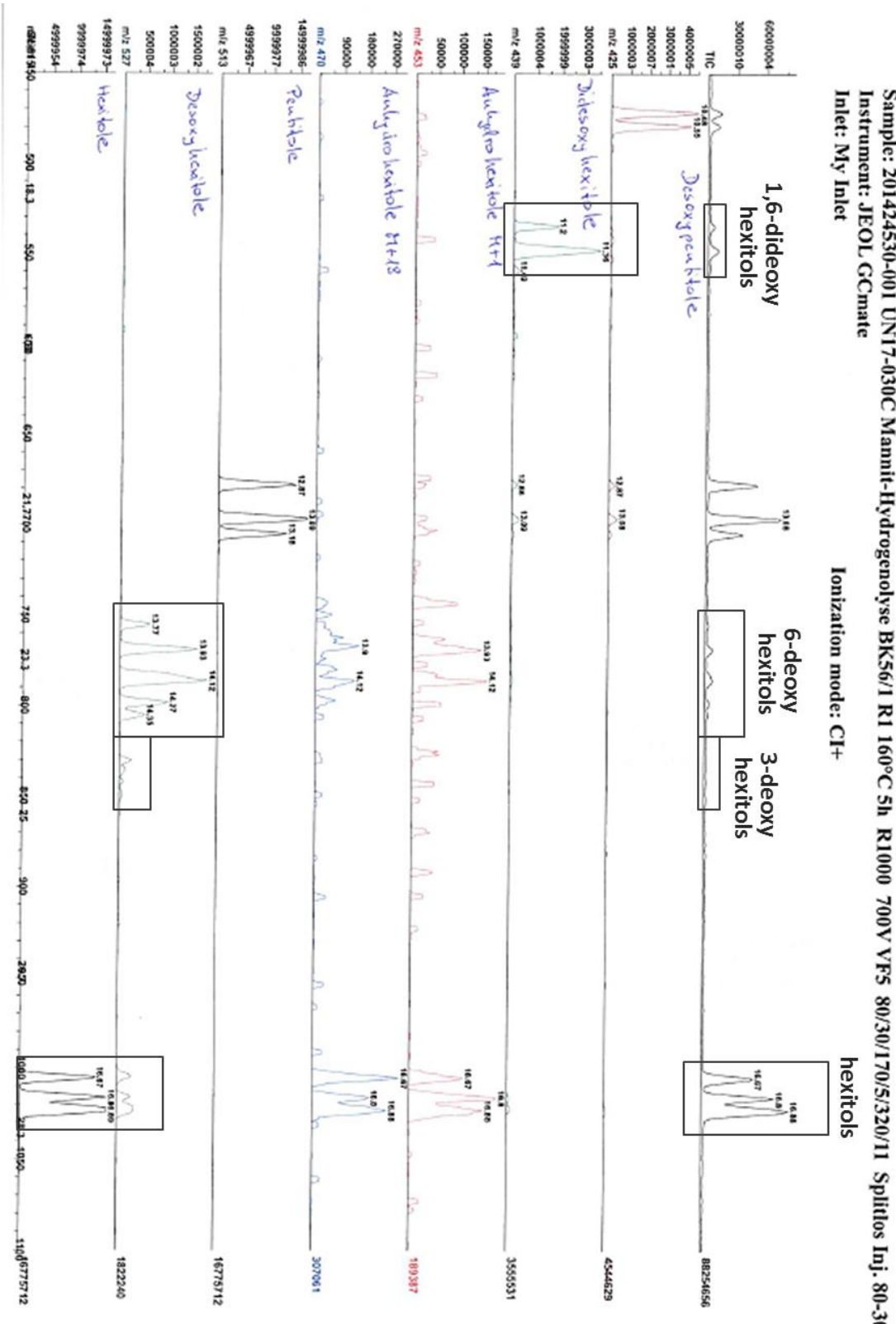



**Figure S-6:** GC-MS analysis of the polyol mixture shown in **Figure S-5**. The 6-deoxy hexitols (labeled as Desoxyhexitole) are detected with a mass-to-charge-ratio of 527 m/z which accounts for the M+1 form (with an added proton) of the TMS-derivatives (see experimental section for silylation). The M+1 species of the 1,6-deoxy hexitols (as Didesoxyhexitole) are detected with a 439 m/z ratio. Identification of 6-deoxy hexitols was performed using the hydrogenation product of rhamnose (6-deoxy sugar). 3-deoxy and dideoxy hexitols were identified using NMR analysis, which was published in a previous work (DOI: 10.1039/C7CY02426F).

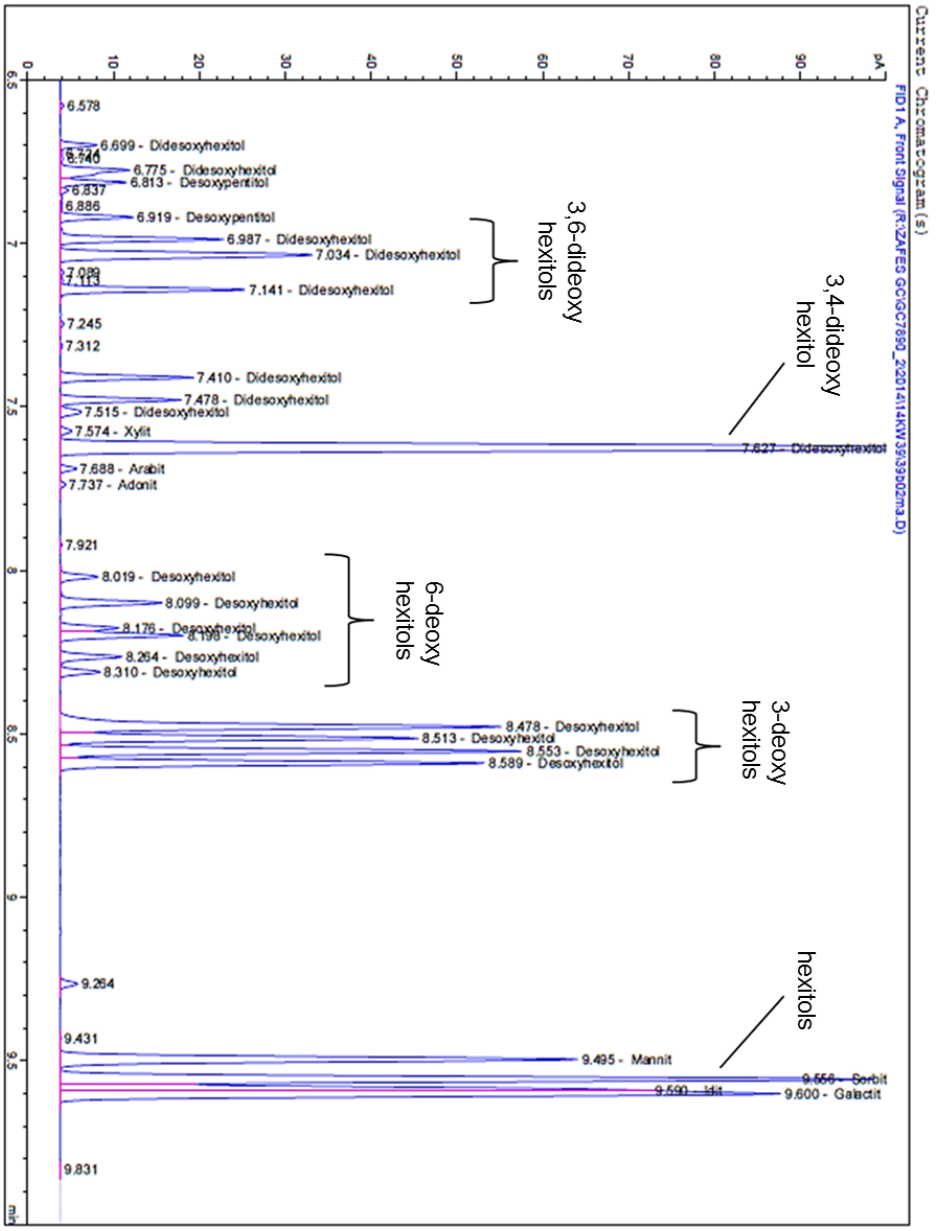



**Figure S-7:** GC chromatogram of the product mixture obtained from conversion of mannitol (aqueous 7.5 wt-% mannitol solution) over Cu-Raney at 180 °C, 150 bar $H_2$ and 5 h reaction time. Four stereoisomers of 3-deoxy hexitols (1,2,4,5,6-hexanepentols) are detected at 8.5 to 8.6 min retention time. Six stereoisomers of 6-deoxy hexitols (1,2,3,4,5-hexanepentols) are detected at 8.0 to 8.3 min, a 3,4-dideoxy hexitol (1,2,5,6-hexanetetrol) at 7.6 min, and three 3,6-dideoxy hexitols (1,2,4,5-hexanetetrol) at 7.0 to 7.2 min retention time. GC-MS and NMR analysis for identification of these products was published in a previous work (DOI: 10.1039/C7CY02426F).

**GC data for identification of products from 1,2,6-hexanetriol hydrogenolysis is shown in Figures S-8 and S-9.**

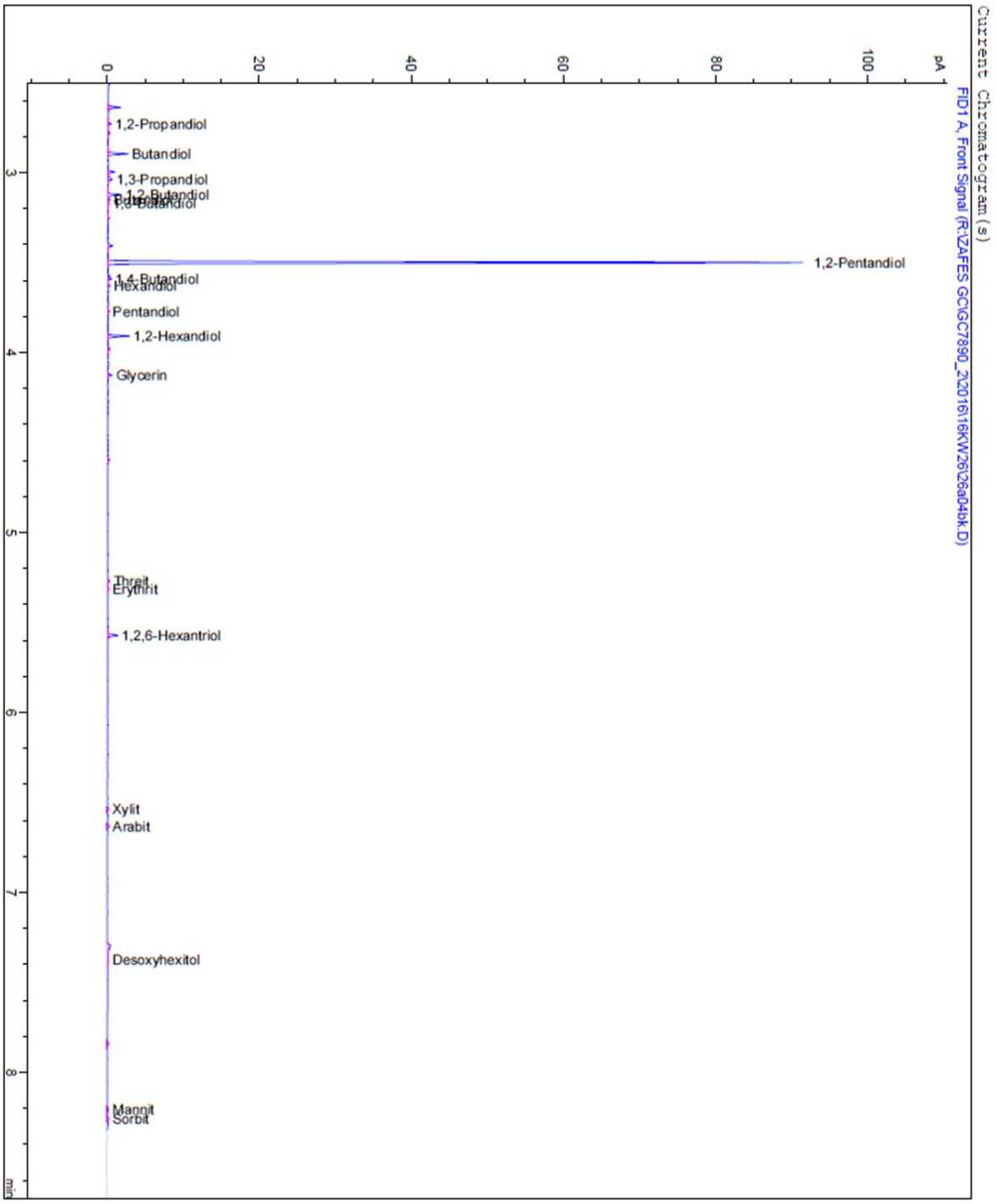



**Figure S-8:** GC chromatogram of the product mixture obtained from conversion of 1,2,6-hexanetriol (aqueous 7.5 wt-% 1,2,6-hexanetriol solution) over $Ru/Al_2O_3$ at 180 °C, 150 bar $H_2$ and 2.5 h reaction time. The only hydrogenolysis product in large amounts is 1,2-pentanediol at 3.5 min retention time.

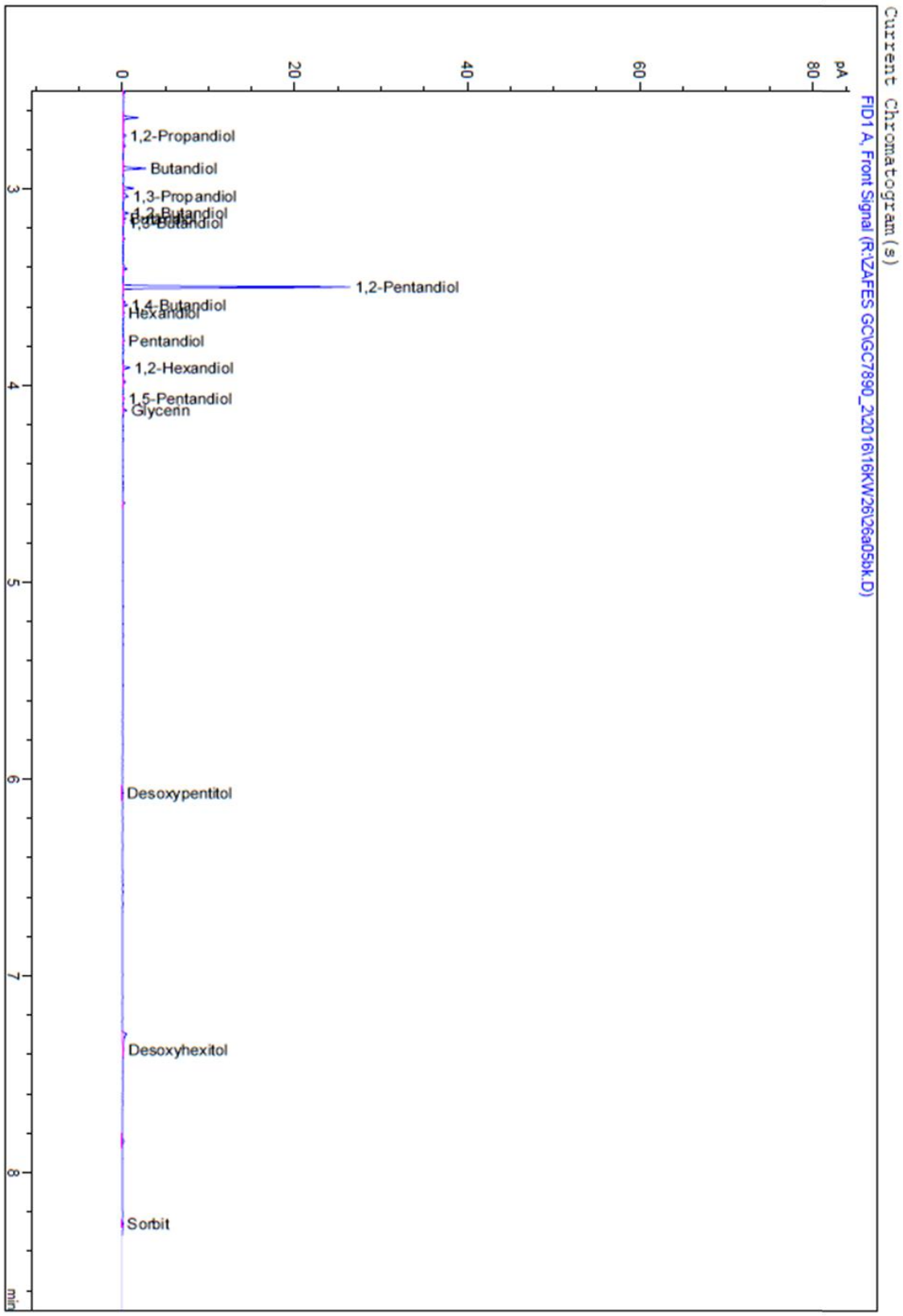
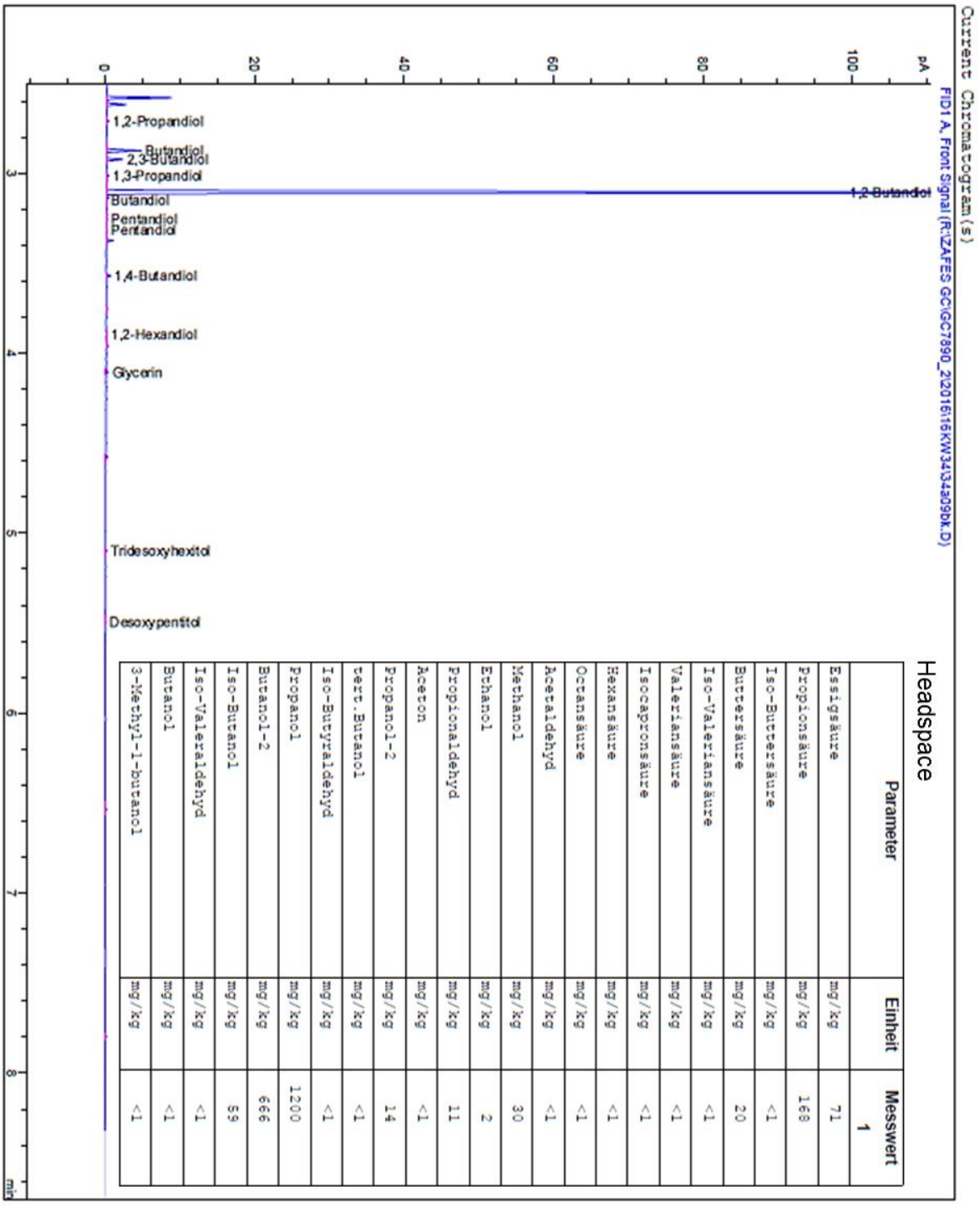



**Figure S-9:** GC chromatogram of the product mixture obtained from conversion of 1,2,6-hexanetriol (aqueous 7.5 wt-% 1,2,6-hexanetriol solution) over $Ru/Al_2O_3$ at 180 °C, 150 bar $H_2$ and 5 h reaction time. The only hydrogenolysis product in large amounts is 1,2-pentanediol at 3.5 min retention time.

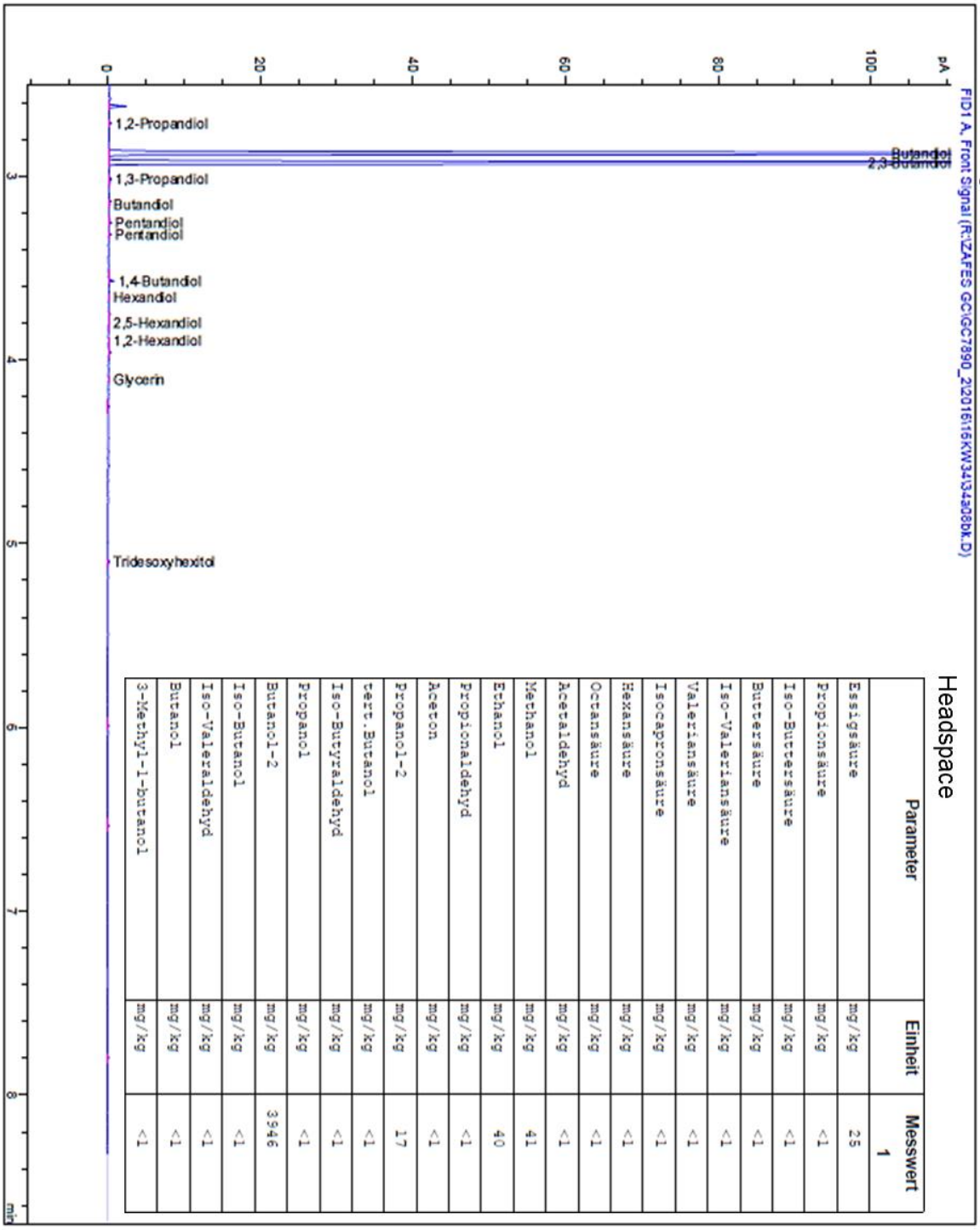
**GC data and headspace analysis for identification of products from hydrogenolysis of 1,2- and 2,3-butanediol is shown in Figures S-10 and S-11.**




Headspace

| Parameter | Einheit | Messwert 1 |
|---|---|---|
| Essigsäure | mg/kg | 71 |
| Propionsäure | mg/kg | 168 |
| Iso-Buttersäure | mg/kg | <1 |
| Buttersäure | mg/kg | 20 |
| Iso-Valeriansäure | mg/kg | <1 |
| Valeriansäure | mg/kg | <1 |
| Isocapronsäure | mg/kg | <1 |
| Hexansäure | mg/kg | <1 |
| Octansäure | mg/kg | <1 |
| Acetaldehyd | mg/kg | <1 |
| Methanol | mg/kg | 30 |
| Ethanol | mg/kg | 2 |
| Propionaldehyd | mg/kg | 11 |
| Aceton | mg/kg | <1 |
| Propanol-2 | mg/kg | 14 |
| tert.Butanol | mg/kg | <1 |
| Iso-Butyraldehyd | mg/kg | <1 |
| Propanol | mg/kg | 1200 |
| Butanol-2 | mg/kg | 666 |
| Iso-Butanol | mg/kg | 59 |
| Iso-Valeraldehyd | mg/kg | <1 |
| Butanol | mg/kg | <1 |
| 3-Methyl-1-butanol | mg/kg | <1 |

**Figure S-10:** GC chromatogram and headspace analysis (for detection of mono alcohols) of the product mixture obtained from conversion of 1,2-butanediol (aqueous 7.5 wt-% 1,2-butanediol solution) over $Ru/Al_2O_3$ at 180 °C, 150 bar $H_2$ and 5 h reaction time. Negligible trace amounts of 1,2-propanediol at 2.7 min retention time are detected. The main product is 1-propanol as shown in the headspace analysis.




Headspace

| Parameter | Einheit | Messwert 1 |
|---|---|---|
| Essigsäure | mg/kg | 25 |
| Propionsäure | mg/kg | <1 |
| Iso-Buttersäure | mg/kg | <1 |
| Buttersäure | mg/kg | <1 |
| Iso-Valeriansäure | mg/kg | <1 |
| Valeriansäure | mg/kg | <1 |
| Isocapronsäure | mg/kg | <1 |
| Hexansäure | mg/kg | <1 |
| Octansäure | mg/kg | <1 |
| Acetaldehyd | mg/kg | <1 |
| Methanol | mg/kg | 41 |
| Ethanol | mg/kg | 40 |
| Propionaldehyd | mg/kg | <1 |
| Aceton | mg/kg | <1 |
| Propanol-2 | mg/kg | 17 |
| tert.Butanol | mg/kg | <1 |
| Iso-Butyraldehyd | mg/kg | <1 |
| Propanol | mg/kg | <1 |
| Butanol-2 | mg/kg | 3946 |
| Iso-Butanol | mg/kg | <1 |
| Iso-Valeraldehyd | mg/kg | <1 |
| Butanol | mg/kg | <1 |
| 3-Methyl-1-butanol | mg/kg | <1 |

**Figure S-11:** GC chromatogram and headspace analysis (for detection of mono alcohols) of the product mixture obtained from conversion of 2,3-butanediol (aqueous 7.5 wt-% 2,3-butanediol solution) over $Ru/Al_2O_3$ at 180 °C, 150 bar $H_2$ and 5 h reaction time. Negligible trace amounts of 1,2-propanediol at 2.7 min retention time are detected. The main product is 2-butanol as shown in the headspace analysis.

## Full set of selectivities for each product (diols, triols, tetraols, pentaols, and hexitols) in Tables S-1 to S-4.

**Table S-1:** Full set of yielded products (each diol, glycerol, deoxytetraols, dideoxypentitols, trideoxyhexitols, tetritols, deoxypentitols, dideoxyhexitols, pentitols, deoxyhexitols, and hexitols) with selectivities for the hydrogenolysis of mannitol over $Ru/Al_2O_3$ at 160 to 220 °C, 150 bar $H_2$ and 5 h reaction time (see **Fig. 3-1** in the main text).

| | | **Catalyst** | **Ru/Al2O3** | | |
|---|---|---|---|---|---|
| | | **Temperature / Reaction time** | 160°C / 5h | 190°C / 5h | 220°C / 5h |
| | | **Component** | molar C yield / % | molar C yield / % | molar C yield / % |
| **Diols** | **C2** | Ethanediol | 0,3 | 1,1 | 0,2 |
| | **C3** | 1,2-Propanediol | 0,4 | 4,3 | 1,5 |
| | | 1,3-Propanediol | 0,5 | 0 | 0 |
| | **C4** | 1,2-Butanediol | 0,9 | 1,6 | 2,4 |
| | | 2,3-Butanediol | 0 | 0,1 | 0,1 |
| | | 1,4-Butanediol | 0,1 | 0,2 | 0,3 |
| | | Other Butanediols / Dideoxytetritols | 0,6 | 1,2 | 1,7 |
| | **C5** | 1,2-Pentanediol | 0,1 | 0,3 | 0,5 |
| | | 1,5-Pentanediol | 0 | 0 | 0 |
| | | Other Pentanediols / Trideoxypentitols | 0,2 | 0,8 | 1,4 |
| | **C6** | 1,2-Hexanediol | 0 | 0 | 0 |
| | | 1,6-Hexanediol | 0 | 0 | 0 |
| | | Other Hexanediols / Tetradeoxyhexitols | 0,5 | 0,4 | 0,4 |
| **Triols** | **C3** | Glycerol | 1,6 | 4,6 | 0,6 |
| | **C4** | 1,2,4-butanetriol | 0 | 0 | 0 |
| | | Butanetriols / Deoxytetrols | 2,4 | 1,1 | 0,3 |
| | **C5** | 1,2,5-pentanetriol | 0 | 0 | 0 |
| | | Pentanetriols / Dideoxypentitols | 1,7 | 0,3 | 0,0 |
| | **C6** | 1,2,6-hexanetriol | 0 | 0 | 0 |
| | | Hexanetriols / Trideoxyhexitols | 0,5 | 0,4 | 0,3 |
| **Tetraols** | **C4** | Threitol | 3,2 | 1,8 | 0,1 |
| | | Erythritol | 2,7 | 2,2 | 0,2 |
| | **C5** | Pentanetetrols / Deoxypentitols | 4,1 | 0,6 | 0,0 |
| | **C6** | 1,2,5,6-hexanetetrol | 0 | 0 | 0 |
| | | 2,3,4,5-hexanetetrol | 2,1 | 0,8 | 0 |
| | | Hexanetetrols / Dideoxyhexitols | 0,2 | 0,1 | 0 |
| **Pentaols** | **C5** | Xylitol | 4,9 | 1,3 | 0,0 |
| | | Arabitol | 8,2 | 5,1 | 0,2 |
| | | Ribitol | 2,6 | 0,6 | 0,0 |
| | **C6** | Hexanepentols / Deoxyhexitols | 6,6 | 1,1 | 0,1 |
| **Hexitols** | **C6** | Mannitol (Reactant) | 5,1 | 14,5 | 2,1 |
| | | Sorbitol | 7,0 | 5,6 | 0,2 |
| | | Iditol | 4,5 | 0,6 | 0,0 |
| | | Galactitol | 5,0 | 0,6 | 0,0 |
| | | **$Y_{C,\ all\ components}$ / %** | 66 | 51 | 13 |
| | | **$X_C$ / %** | 78 | 79 | 98 |

| **Categorization into product groups** | 160°C / 5h | 190°C / 5h | 220°C / 5h |
|---|---|---|---|
| S (deoxy C6)* / % | 13,1 | 3,4 | 0,8 |
| S (C5)* / % | 27,8 | 11,5 | 2,3 |
| S (C4)* / % | 12,8 | 10,4 | 5,2 |
| S (C3)* / % | 3,1 | 11,3 | 2,2 |
| S (C2)* / % | 0,4 | 1,4 | 0,2 |

* deoxy C6: includes deoxy, dideoxy, trideoxy and tetradeoxy C6 products
* C5: includes deoxy, dideoxy and trideoxy C5 products
* C4: includes deoxy and dideoxy C4 products
* C3: includes deoxy C3 products

**Table S-2:** Full set of yielded products (each diol, glycerol, deoxytetraols, dideoxypentitols, trideoxyhexitols, tetritols, deoxypentitols, dideoxyhexitols, pentitols, deoxyhexitols, and hexitols) with selectivities for the hydrogenolysis of mannitol over Ru/C at 160 to 220 °C, 150 bar $H_2$ and 5 h reaction time (see **Fig. 3-1** in the main text).

| | | **Catalyst** | **Ru/C** | | |
|---|---|---|---|---|---|
| | | **Temperature / Reaction time** | 160°C / 5h | 190°C / 5h | 220°C / 5h |
| | | **Component** | molar C yield / % | molar C yield / % | molar C yield / % |
| **Diols** | **C2** | Ethanediol | 0,3 | 1,2 | 2,2 |
| | **C3** | 1,2-Propanediol | 0,5 | 1,9 | 6,3 |
| | | 1,3-Propanediol | 0,3 | 0 | 0 |
| | **C4** | 1,2-Butanediol | 0,9 | 1,0 | 2,5 |
| | | 2,3-Butanediol | 0,0 | 0,0 | 0,1 |
| | | 1,4-Butanediol | 0,1 | 0,1 | 0,3 |
| | | Other Butanediols / Dideoxytetritols | 0,6 | 0,8 | 1,8 |
| | **C5** | 1,2-Pentanediol | 0,1 | 0,3 | 0,6 |
| | | 1,5-Pentanediol | 0 | 0 | 0 |
| | | Other Pentanediols / Trideoxypentitols | 0,2 | 0,9 | 1,9 |
| | **C6** | 1,2-Hexanediol | 0 | 0,1 | 0,1 |
| | | 1,6-Hexanediol | 0 | 0 | 0 |
| | | Other Hexanediols / Tetradeoxyhexitols | 0,1 | 0,8 | 1,8 |
| **Triols** | **C3** | Glycerol | 1,9 | 4,3 | 2,8 |
| | **C4** | 1,2,4-butanetriol | 0 | 0 | 0 |
| | | Butanetriols / Deoxytetrols | 1,2 | 1,0 | 0,2 |
| | **C5** | 1,2,5-pentanetriol | 0 | 0 | 0 |
| | | Pentanetriols / Dideoxypentitols | 2,1 | 0,5 | 0,4 |
| | **C6** | 1,2,6-hexanetriol | 0 | 0 | 0 |
| | | Hexanetriols / Trideoxyhexitols | 0,2 | 0,1 | 1,9 |
| **Tetraols** | **C4** | Threitol | 4,1 | 5,8 | 1,7 |
| | | Erythritol | 3,4 | 4,7 | 1,5 |
| | **C5** | Pentanetetrols / Deoxypentitols | 2,9 | 1,3 | 0,3 |
| | **C6** | 1,2,5,6-hexanetetrol | 0 | 0 | 0 |
| | | 2,3,4,5-hexanetetrol | 2,3 | 0,7 | 0,4 |
| | | Hexanetetrols / Dideoxyhexitols | 0,2 | 0,1 | 0 |
| **Pentaols** | **C5** | Xylitol | 6,5 | 5,3 | 1,4 |
| | | Arabitol | 11,0 | 8,5 | 2,5 |
| | | Ribitol | 3,7 | 2,8 | 0,4 |
| | **C6** | Hexanepentols / Deoxyhexitols | 3,5 | 1,7 | 0,2 |
| **Hexitols** | **C6** | Mannitol (Reactant) | 6,5 | 2,8 | 2,2 |
| | | Sorbitol | 9,3 | 4,5 | 2,3 |
| | | Iditol | 6,0 | 2,9 | 0,4 |
| | | Galactitol | 8,9 | 3,3 | 0,0 |
| | | **$Y_{C,\ all\ components}$ / %** | 77 | 58 | 40 |
| | | **$X_C$ / %** | 69 | 87 | 95 |

| **Categorization into product groups** | 160°C / 5h | 190°C / 5h | 220°C / 5h |
|---|---|---|---|
| S (deoxy C6)* / % | 9,2 | 4,3 | 7,8 |
| S (C5)* / % | 38,1 | 22,6 | 8,0 |
| S (C4)* / % | 14,9 | 15,6 | 8,6 |
| S (C3)* / % | 3,7 | 7,1 | 9,6 |
| S (C2)* / % | 0,5 | 1,4 | 2,3 |

* deoxy C6: includes deoxy, dideoxy, trideoxy and tetradeoxy C6 products
* C5: includes deoxy, dideoxy and trideoxy C5 products
* C4: includes deoxy and dideoxy C4 products
* C3: includes deoxy C3 products

**Table S-3:** Full set of yielded products (each diol, glycerol, deoxytetraols, dideoxypentitols, trideoxyhexitols, tetritols, deoxypentitols, dideoxyhexitols, pentitols, deoxyhexitols, and hexitols) with selectivities for the hydrogenolysis of mannitol over $Ru/Al_2O_3$ at 160 °C, 150 bar $H_2$ and 10 h reaction time, with samples taken every 2.5 h (see **Fig. 3-3** in the main text).

| | | **Catalyst** | **Ru/Al2O3** | | | | |
|---|---|---|---|---|---|---|---|
| | | **Temperature / Reaction time** | 160°C 0h | 160°C 2,5h | 160°C 5h | 160°C 7,5h | 160°C 10h |
| | | **Component** | molar C yield / % | molar C yield / % | molar C yield / % | molar C yield / % | molar C yield / % |
| **Diols** | **C2** | Ethanediol | 0 | 1,0 | 1,1 | 0,8 | 0,6 |
| | **C3** | 1,2-Propanediol | 0 | 2,1 | 3,4 | 3,3 | 3,6 |
| | | 1,3-Propanediol | 0 | 0 | 0 | 0,3 | 0 |
| | **C4** | 1,2-Butanediol | 0 | 0,1 | 1,0 | 0 | 0,5 |
| | | 2,3-Butanediol | 0 | 0 | 0 | 0 | 0 |
| | | 1,4-Butanediol | 0 | 0 | 0,1 | 0 | 0,1 |
| | | Other Butanediols / Dideoxytetritols | 0 | 0,1 | 0,7 | 0 | 0,4 |
| | **C5** | 1,2-Pentanediol | 0 | 0 | 0 | 0 | 0,2 |
| | | 1,5-Pentanediol | 0 | 0 | 0 | 0 | 0 |
| | | Other Pentanediols / Trideoxypentitols | 0 | 0 | 0 | 0 | 0,7 |
| | **C6** | 1,2-Hexanediol | 0 | 0 | 0 | 0 | 0 |
| | | 1,6-Hexanediol | 0 | 0 | 0 | 0 | 0 |
| | | Other Hexanediols / Tetradeoxyhexitols | 0 | 0 | 0 | 0 | 0,6 |
| **Triols** | **C3** | Glycerol | 0 | 4,7 | 4,8 | 3,4 | 2,7 |
| | **C4** | 1,2,4-butanetriol | 0 | 0 | 0 | 0 | 0 |
| | | Butanetriols / Deoxytetrols | 0 | 1,7 | 1,6 | 1,6 | 1,3 |
| | **C5** | 1,2,5-pentanetriol | 0 | 0 | 0 | 0 | 0 |
| | | Pentanetriols / Dideoxypentitols | 0 | 0,5 | 0 | 0,9 | 0,9 |
| | **C6** | 1,2,6-hexanetriol | 0 | 0 | 0 | 0 | 0 |
| | | Hexanetriols / Trideoxyhexitols | 0 | 0,4 | 0 | 0 | 0,4 |
| **Tetraols** | **C4** | Threitol | 0 | 4,6 | 3,7 | 2,7 | 2,0 |
| | | Erythritol | 0 | 3,7 | 2,9 | 2,1 | 1,6 |
| | **C5** | Pentanetetrols / Deoxypentitols | 0 | 2,0 | 1,2 | 1,4 | 0,9 |
| | **C6** | 1,2,5,6-hexanetetrol | 0 | 0 | 0 | 0 | 0 |
| | | 2,3,4,5-hexanetetrol | 0 | 1,5 | 0,6 | 0,7 | 0,6 |
| | | Hexanetetrols / Dideoxyhexitols | 0 | 0,2 | 0,1 | 0,1 | 0,1 |
| **Pentaols** | **C5** | Xylitol | 0 | 4,1 | 2,5 | 1,6 | 1,1 |
| | | Arabitol | 0 | 7,2 | 4,1 | 2,7 | 1,9 |
| | | Ribitol | 0 | 1,6 | 1,0 | 0,7 | 0,4 |
| | **C6** | Hexanepentols / Deoxyhexitols | 0 | 2,5 | 1,5 | 1,2 | 0,5 |
| **Hexitols** | **C6** | Mannitol (Reactant) | 100 | 5,2 | 2,3 | 1,5 | 1,1 |
| | | Sorbitol | 0 | 5,3 | 2,5 | 1,5 | 1,0 |
| | | Iditol | 0 | 2,6 | 1,4 | 0,8 | 0,5 |
| | | Galactitol | 0 | 1,6 | 0,7 | 0,5 | 0,3 |
| | | **$Y_{C,\ all\ components}$ / %** | 100 | 53 | 37 | 28 | 24 |
| | | **$X_C$ / %** | 0 | 85 | 93 | 96 | 97 |

**Categorization into product groups**

| fraction / mol-% | 160°C / 0h | 160°C / 2,5h | 160°C / 5h | 160°C / 7,5h | 160°C / 10h |
|---|---|---|---|---|---|
| C6 | 100 | 14,6 | 6,9 | 4,3 | 2,9 |
| C5 | 0 | 15,5 | 9,4 | 7,0 | 6,2 |
| C4 | 0 | 10,1 | 10,0 | 6,4 | 5,8 |
| C3 | 0 | 6,8 | 8,4 | 7,0 | 6,6 |
| C2 | 0 | 1,0 | 1,1 | 0,8 | 0,6 |
| C1 | 0 | 52,0 | 64,3 | 74,5 | 77,8 |
| deoxy C6 * | 0 | 2,5 | 2,4 | 1,2 | 0,5 |
| deoxy C5 * | 0 | 2,0 | 1,9 | 1,1 | 0,9 |

* deoxy C6: includes only monodeoxy C6 products

* deoxy C5: includes only monodeoxy C5 products

**Table S-4:** Full set of yielded products (each diol, glycerol, deoxytetraols, dideoxypentitols, trideoxyhexitols, tetritols, deoxypentitols, dideoxyhexitols, pentitols, deoxyhexitols, and hexitols) with selectivities for the hydrogenolysis of mannitol, 1,2,3,4,5-hexanepentol, 1,2,6-hexanetriol, and isosorbide over $Ru/Al_2O_3$ at 180 °C, 150 bar $H_2$ and 5 h reaction time (the1,2,6-hexanetriol sample was taken after 2,5 h reaction time, see **Table 3-1** in the main text).

| | | **Catalyst** | **Ru/Al2O3** | | | |
|---|---|---|---|---|---|---|
| | | **Temperature / Reaction time** | 180°C / 5h | 180°C / 5h | 180°C / 2,5h | 180°C / 5h |
| | | **Reactant** | Mannitol | 1,2,3,4,5-Hexanepentol | 1,2,6-Hexanetriol | Isosorbide |
| | | **Component** | molar C yield / % | molar C yield / % | molar C yield / % | molar C yield / % |
| **Diols** | **C2** | Ethanediol | 1,1 | 0 | 0 | 0 |
| | **C3** | 1,2-Propanediol | 3,5 | 3,1 | 0 | 0 |
| | | 1,3-Propanediol | 0,2 | 0 | 0,2 | 0 |
| | **C4** | 1,2-Butanediol | 1,8 | 0,3 | 0,5 | 0,1 |
| | | 2,3-Butanediol | 0 | 1,8 | 0 | 0 |
| | | 1,4-Butanediol | 0,2 | 0,1 | 0,1 | 0,1 |
| | | Other Butanediols / Dideoxytetritols | 1,3 | 2,4 | 0,8 | 0,9 |
| | **C5** | 1,2-Pentanediol | 0,1 | 0 | 30,7 | 0 |
| | | 1,5-Pentanediol | 0 | 0 | 0 | 0 |
| | | Other Pentanediols / Trideoxypentitols | 0,4 | 1,0 | 0 | 0 |
| | **C6** | 1,2-Hexanediol | 0 | 0 | 1,1 | 0 |
| | | 1,6-Hexanediol | 0 | 0 | 0 | 0 |
| | | Other Hexanediols / Tetradeoxyhexitols | 0,3 | 2,5 | 0 | 0,3 |
| **Triols** | **C3** | Glycerol | 4,8 | 0,3 | 0 | 0 |
| | **C4** | 1,2,4-butanetriol | 0 | 0 | 0 | 0 |
| | | Butanetriols / Deoxytetrols | 1,6 | 3,9 | 0 | 0 |
| | **C5** | 1,2,5-pentanetriol | 0 | 0 | 0 | 0 |
| | | Pentanetriols / Dideoxypentitols | 0,5 | 0 | 0 | 0,2 |
| | **C6** | 1,2,6-hexanetriol | 0 | 0 | 0,5 | 0 |
| | | Hexanetriols / Trideoxyhexitols | 0,5 | 0,9 | 0 | 0 |
| **Tetraols** | **C4** | Threitol | 3,7 | 0 | 0 | 0 |
| | | Erythritol | 2,9 | 0 | 0 | 0 |
| | **C5** | Pentanetetrols / Deoxypentitols | 1,4 | 4,4 | 0 | 0 |
| | **C6** | 1,2,5,6-hexanetetrol | 0 | 0 | 0 | 0 |
| | | 2,3,4,5-hexanetetrol | 0,6 | 0,9 | 0 | 0 |
| | | Hexanetetrols / Dideoxyhexitols | 0,1 | 0,1 | 0 | 0 |
| **Pentaols** | **C5** | Xylitol | 2,5 | 0 | 0 | 0 |
| | | Arabitol | 4,2 | 0 | 0 | 0 |
| | | Ribitol | 0,9 | 0 | 0 | 0 |
| | **C6** | Hexanepentols / Deoxyhexitols | 1,4 | 4,8 | 0 | 0 |
| **Cyclic** | **C6** | Anhydrohexitol | 0 | 0 | 0 | 0 |
| | | Isosorbide | 0 | 0 | 0 | 20,3 |
| | | Dianhydrohexitol isomers | 0 | 0 | 0 | 31,2 |
| **Hexitols** | **C6** | Mannitol (Reactant) | 2,3 | 0 | 0 | 0 |
| | | Sorbitol | 2,6 | 0 | 0 | 0 |
| | | Iditol | 1,3 | 0 | 0 | 0 |
| | | Galactitol | 0,7 | 0 | 0 | 0 |
| | | **$Y_{C,\ all\ components}$ / %** | 41 | 26 | 34 | 53 |
| | | **$X_C$ / %** | 93 | 96 | 99 | 59 |