Electronic Supplementary Material (ESI) for Green Chemistry.

ELECTRONIC SUPPLEMENTARY INFORMATION

Towards a greener synthesis of dianhydrohexitol esters

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Fig. S1 Dean-Stark apparatus for the esterification using Route 1

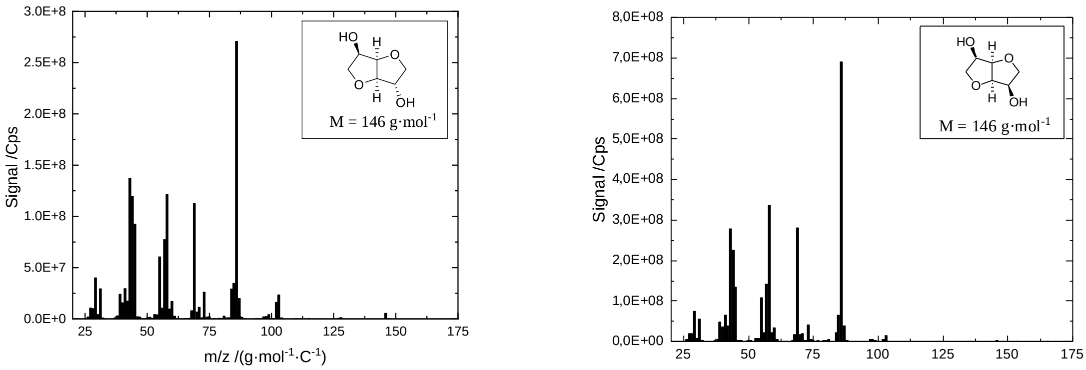

Fig. S2 Mass spectra of isosorbide (left) and isomannide (right)

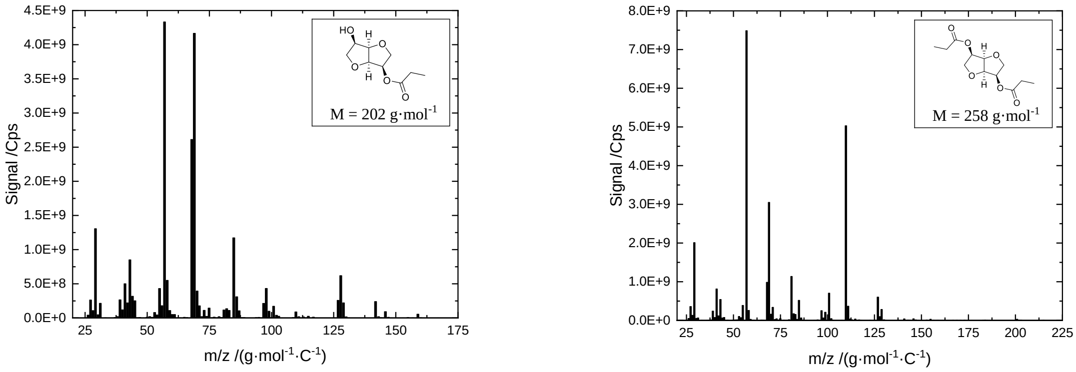

Fig. S3 Mass spectra of isomannide monoester 2-propionyl isomannide (left) and diester 2,5-dipropionyl isomannide (right); there were no further peaks beyond 175 and 225 $gmol^{-1}C^{-1}$

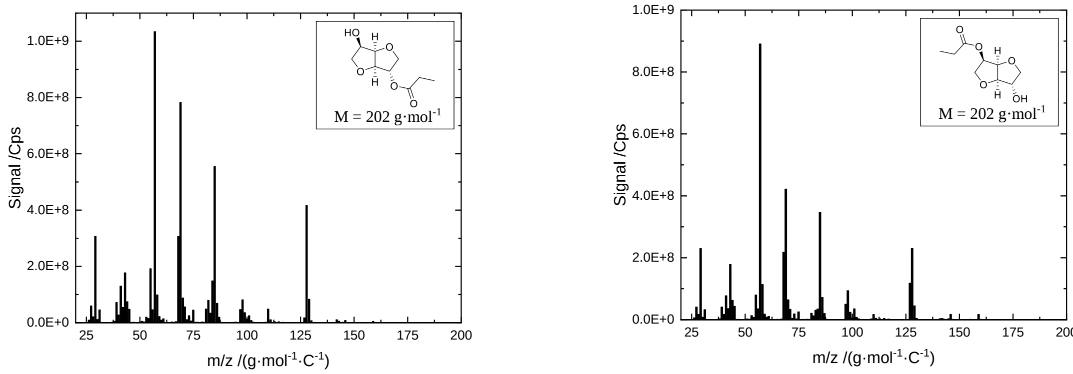

Fig. S4 Mass spectra of isosorbide monoesters 2-propionyl isosorbide (left) and 5-propionyl isosorbide (right); there were no further peaks beyond 200 gmol^{-1}C^{-1}

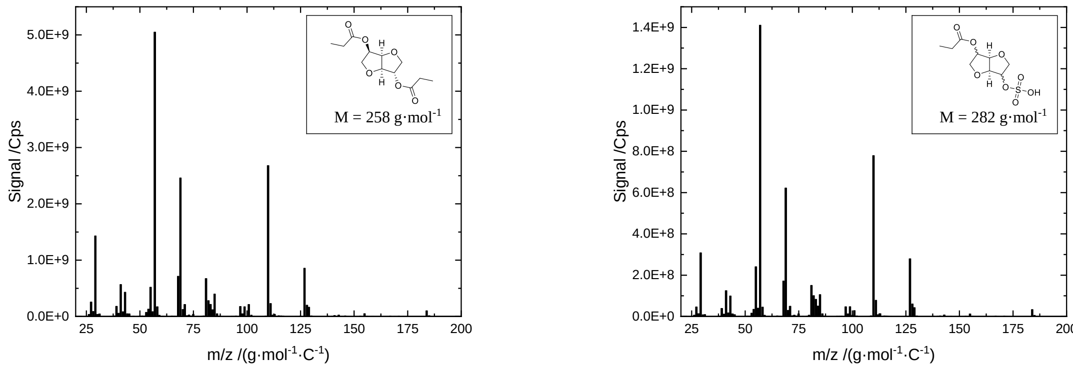

Fig. S5 Mass spectra of isosorbide diester 2,5-dipropionyl isosorbide (left) and byproduct 5-propionyl-2-sulfon isosorbide (right); there were no further peaks beyond 200 gmol^{-1}C^{-1}

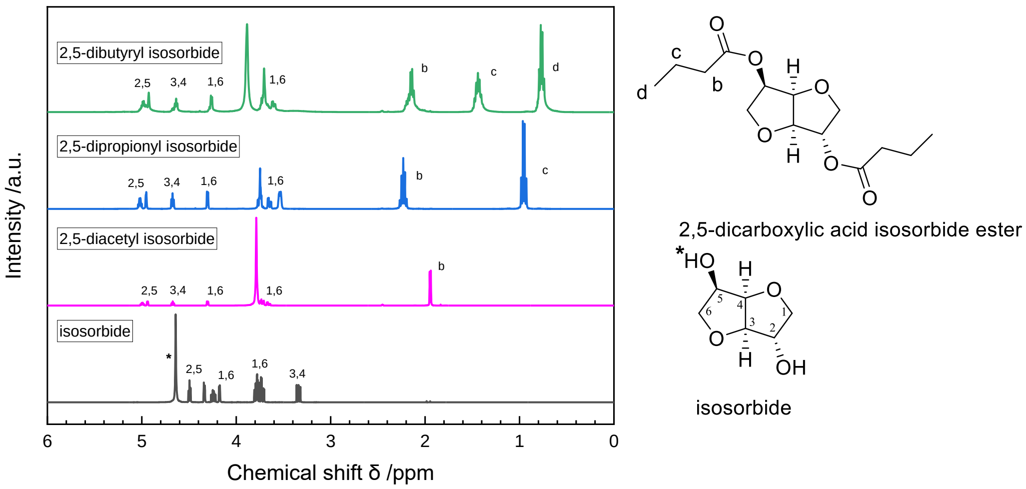

Fig. S6 ^{1}H NMR spectra of isosorbide (educt), 2,5-diacetyl isosorbide, 2,5-dipropionyl isosorbide and 2,5-dibutyryl isosorbide

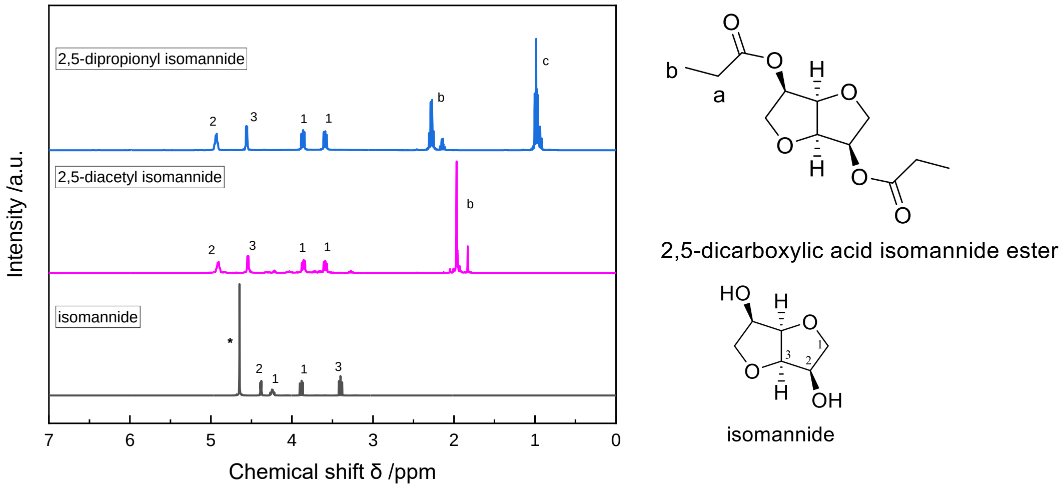

Fig. S7 [1]H NMR spectra of isomannide, 2,5-diacetyl isomannide and 2,5-dipropionyl isomannide

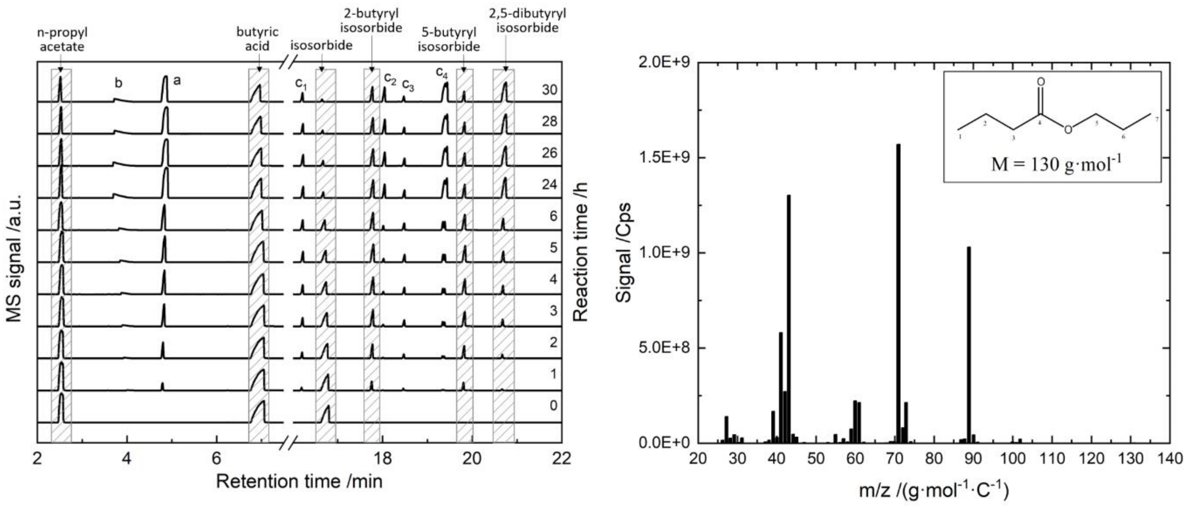

Fig. S8 Reaction progress for the esterification of isosorbide with butyric acid: gas chromatograms of esterification of isosorbide with entrainer n-propyl acetate, mass spectra of the new peak ‘a’ at retention time 4.4 min indicating butyric acid propyl ester (right)

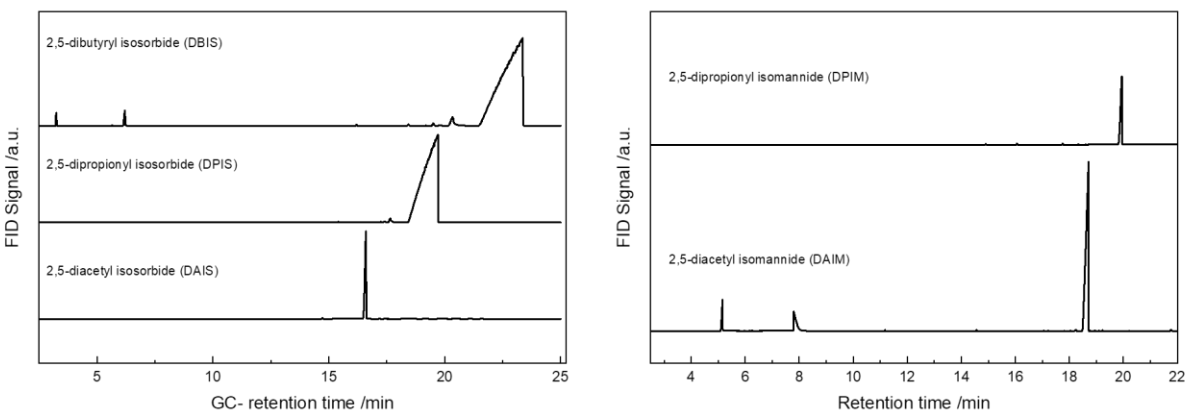

Fig. S9 Gas chromatograms of the purified dianhydrohexitol esters

OpenLCA data

Tab. S1 Elementary or process flows of chemicals and energy quantities for the production of 1000 kg DAIS; implemented processes are based on literature data; ecoinvent based product and elementary flows already contain the pre-processes from cradle-to-gate; output elementary flows are emissions which leave the product system under study and cause emissions and accordingly environmental impacts

Elementary or process flow	**Quantity for the production of 1t DAIS**	**Data source /Ecoinvent flows and processes used as input and output data for the openLCA impact assessment**
Inputs Route 1		
Isosorbide	648.5kg	Implemented process based on literature data [1-4]
Glucose	1024.00 kg	Manufacture of starches and starch products: glucose production | glucose | Cutoff, U - GLO
Hydrogen, liquid	11.41 kg	Manufacture of basic chemicals: market for hydrogen, liquid | hydrogen, liquid | Cutoff, U - RER
Water, deionised	1530.61 kg	Water collection, treatment and supply: market for water, deionised | water, deionised | Cutoff, U - Europe without Switzerland
Energy for the catalytic hydrogenation of glucose to sorbitol	9776.26 kWh	Electric power generation, transmission and electricity voltage: transformation from high to medium voltage | electricity, medium voltage | Cutoff, U - FR
Energy for the dehydration of sorbitol to isosorbide	6607.19 kWh	Electric power generation, transmission and electricity voltage: transformation from high to medium voltage | electricity, medium voltage | Cutoff, U - FR
Energy and heat for the crystallisation of isosorbide	1027.36 kWh	Electric power generation, transmission and electricity voltage: transformation from high to medium voltage | electricity, medium voltage | Cutoff, U - FR
Cooling water	40.53 m^3	Water collection, treatment and supply: market for water, deionised | water, deionised | Cutoff, U - Europe without Switzerland
Acetic acid	1199.74 kg	Manufacture of basic chemicals: market for acetic acid, without water, in 98 % solution state | acetic acid, without water, in 98 % solution state | Cutoff, U - GLO
Amberlyst-15 (wet)	31.74 kg	Implemented process based on literature data [5]
Styrene	23.15 kg	Manufacture of plastics and synthetic rubber in primary forms: market for styrene | styrene | Cutoff, U - GLO
Divinylbenzene, produced from styrene and ethylene	3.50 kg	Implemented process based on literature data [6]
water, deionised	37.45 kg	Water collection, treatment and supply: market for water, deionised | water, deionised | Cutoff, U - Europe without Switzerland
Energy: polymerisation and functionalisation	122.51 kWh	Electric power generation, transmission and distribution: electricity voltage transformation from high to medium voltage | electricity, medium voltage | Cutoff, U - DE
sulfuric acid	3.41 kg	Manufacture of basic precious and other non-ferrous metals: market for sulfuric acid | sulfuric acid | Cutoff, U - RER
carboxymethyl cellulose, powder	3.02 kg	Manufacture of basic chemicals: carboxymethyl cellulose production, powder | carboxymethyl cellulose, powder | Cutoff, U - RER
Entrainer: Toluene, liquid n-propylacetate	 Start: 2209.43 kg (recycle: 2099.50 kg) Start: 2260.00 kg (recycle: 2147.00 kg)	 Manufacture of basic chemicals: market for toluene, liquid | toluene, liquid | Cutoff, U – RER Implemented process based on literature data [7]
Energy for chemicals production (pre-processes), for esterification [5], for DAIS purification [5]	20020.32 kWh 10573.58 kWh 3873.64 kWh	Electric power generation, transmission and distribution: electricity voltage transformation from high to medium voltage | electricity, medium voltage | Cutoff, U - DE
Outputs Route 1		
Diacetyl isosorbide (DAIS)	1000.0 kg	set output
Acetic acid	62.8 kg	Elementary Flow: Emission to water/fresh water

Entrainer: Toluene n-Propylacetate	 110.5 kg 113.0 kg	 Elementary Flow: Emission to water/fresh water Elementary Flow: Emission to water/unspecified
Waste water (from esterification)	156.52 kg	Elementary Flow: Emission to water/fresh water
Amberlyst-15 (wet and waste) Polystyrene waste	 31.74 kg	 Elementary Flow: Waste/unspecified
Waste water from Amberlyst production, purification, functionalisation	2568.0 kg	Elementary Flow: Emission to water/fresh water
Waste water from isosorbid production from glucose	74940.0 kg	Elementary Flow: Emission to water/fresh water
Inputs Route 2		
Isosorbide	634.78 kg	Implemented process based on literature data [1-4]
Acetic anhydride	804.8 kg (recycle 566.2 kg)	acetic anhydride production, ketene route | acetic anhydride | Cutoff, U - RER
Water for hydrolysis	10.5 kg	Water collection, treatment and supply: market for water, deionised | water, deionised | Cutoff, U - Europe without Switzerland
Energy for chemicals production (pre-processes), for esterification [5], for DAIS purification [5]	31927.67 kWh 1162.08 kWh 3960.66 kWh	electricity voltage transformation from high to medium voltage | electricity, medium voltage | Cutoff, U - DE
Outputs Route 2		
Diacetyl isosorbide	1000.0 kg	set output
Acetic acid	269.33 kg	Elementary Flow: Emission to water/fresh water
Inputs Reference Route		
Isosorbide	634.78 kg	Implemented process based on literature data [1-4]
Acetic acid	1199.74 kg	market for acetic acid, without water, in 98% solution state | acetic acid, without water, in 98% solution state | Cutoff, U - GLO
Sodium bicarbonate ($NaHCO_3$)	950.29 kg	market for sodium bicarbonate | sodium bicarbonate | Cutoff, U - GLO
Sulfuric acid	1.27 kg	market for sulfuric acid | sulfuric acid | Cutoff, U - RER
Toluene	2209.04 kg (recycle 2099.5 kg)	Manufacture of basic chemicals: market for toluene, liquid | toluene, liquid | Cutoff, U - RER
Energy for chemicals production (pre-processes), for esterification [5], for DAIS purification [5]	 28479.14 kWh 9163.77 kWh 3874.22 kWh	electricity voltage transformation from high to medium voltage | electricity, medium voltage | Cutoff, U - DE
Outputs Reference Route		
Diacetyl isosorbide	1000.0 kg	set output
Acetic acid	678.0 kg	Elementary Flow: Emission to water/fresh water
Toluene	110.5 kg	Elementary Flow: Emission to water/fresh water
Waste water (containing neutralized sulfuric acid)	11456.5 kg	Elementary Flow: Emission to water/fresh water
Sodium sulfate	1.27 kg	Elementary Flow: Resource/unspecified

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[1] B. A. Rugg, W. Brenner, U.S. Patent No. 4,316,747, 1982.
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[3] J. C Chao, D. T Huibers U.S. Patent No. 4322569, 1982.
[4] D. Schreck, M. Bradford, N. Clinton, P. Arbury, Patent No. WO2009126852, 2009.
[5] P. Akkaramongkolporn, T. Ngawhirunpat, P. Opanasopit, AAPS PharmSciTech, 2009, 10, 641.
[6] Ecoinvent database 3.7.1 “styrene production | styrene | Cutoff, U - RER”.
[7] Ecoinvent database 3.7.1 “propyl acetate production | isopropyl acetate | Cutoff, U – RER.”
[8] T. Fleiter, B. Schlomann, W. Eichhammer, Fraunhofer-Verlag Stuttgart, 2013.