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Hydrogenation of 4-deoxy- β -L-*threo*-hex-4-enopyranosyluronic acid sodium salt attached to xylofucose or xylofucose

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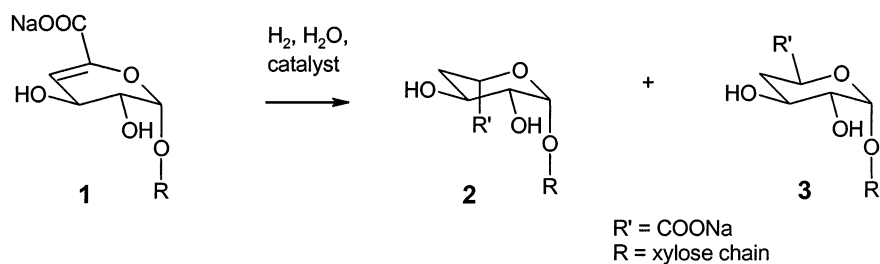
Abstract—A sodium salt of 4-deoxy- β -L-*threo*-hex-4-enopyranosyluronic acid **1** attached to xylofucose or xylofucose is hydrogenated for the first time. Moreover, the double bond of 4-deoxy- β -L-*threo*-hex-4-enopyranosyluronic acid sodium salt **1** can be reduced by hydrogenation in water without removing the allylic hydroxyl group. Highly active homogeneous catalysts and heterogeneous catalysts were tested and only palladium or platinum on charcoal catalysts were found to be active in this case. © 2001 Elsevier Science Ltd. All rights reserved.

The formation of 4-deoxy- β -L-*threo*-hex-4-enopyranosyluronic acid (hexenuronic acid) **1** from 4-*O*-methylglucuronic acid during the drastic alkaline conditions of the kraft pulp process leads to increased consumption of typical bleaching chemicals excluding oxygen and alkaline hydrogen peroxide.¹ The formation of hexenuronic acid **1** also contributes to the kappa number of kraft pulps.² In addition, it may have an effect on yellowing and metal binding properties of pulp.³ The sodium salt of hexenuronic acid **1** is isolated from the enzymatically hydrolyzed birch kraft pulp by anion exchange chromatography.³ The hexenuronic acid **1** side group has many interesting properties. First of all, this compound has a carboxyl group, which causes binding to metals. Moreover, the double bond of this side group has an ability to be oxidized in UV light by oxygen, which most likely causes the yellowing of the final product, paper.

Modification of the double bond of hexenuronic acid **1** has been attempted in different ways, but mostly by

oxidative means. When hexenuronic acid **1** is treated with permanganate in water or mercuric acetate in acidic water, the whole side group breaks off from the xylan chain.² Also, dihydroxylation with the known methods of OsO₄ with NMO⁴ or RuCl₃·xH₂O with NaIO₄⁵ leads to decomposition of the compound, which means that all the positive properties of this compound are lost. Moreover, epoxidation by methyl trioxorhenium with hydrogen peroxide does not work with this compound at all.⁶

The first hydrogenation of an uronic acid type compound was done as early as 1956 with 10% palladium on charcoal by Linker et al.⁷ He assumed that the product was a hydrogenolysis product of the allylic hydroxyl group. However, in this article it is demonstrated that hexenuronic acid **1** can be hydrogenated with heterogeneous catalysts without removing the allylic hydroxyl group (Scheme 1). This reaction results in the formation of 4-deoxy-L-galacturonic acid **2**¹¹ and 4-deoxy-D-galacturonic acid **3**¹² as their sodium salts.



Scheme 1.

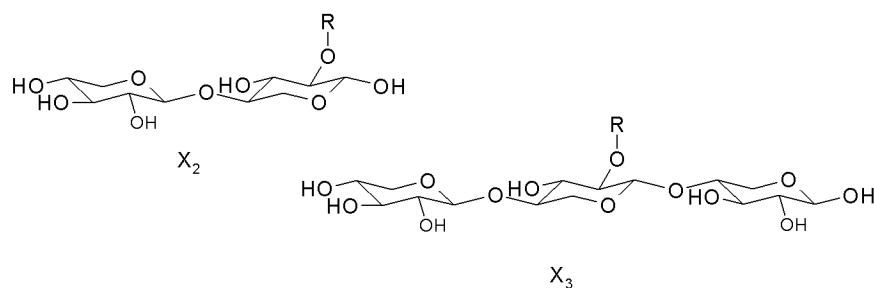
Keywords: hydrogenation; unsaturated acid; heterogeneous catalysis; homogeneous catalysis.

The hexenuronic acids (HexA) employed in these experiments were attached β -(1–2) to xylose. The substrate used in these reactions was a mixture of the hexenuronic acid xylodiose (HexA- X_2) and xylotriose (HexA- X_3) of the xylan chain (Scheme 2).

It was noticed that homogeneous catalysts did not work in this case as can be seen from Table 1 (entries 1–5).⁸ Dendrimer-encapsulated Pd catalyst (G4-OH(Pd₄₀)),⁹ ruthenium catalyst with sulfonated binap ligand [Rh{(R)-binap(SO₃Na)₄}(H₂O)₂]ClO₄,¹⁰ palladium (Pd[(R)-binap(SO₃Na)₄]Cl₂) and platinum (Pt[(R)-binap(SO₃Na)₄]Cl₂) catalysts with sulfonated binap ligand and ruthenium trichloride (RuCl₃·xH₂O) were tried as water soluble catalysts without success. The inactivity of homogeneous catalysts in this case is assumed to be due to the binding of the catalyst metal to the carboxyl group.

Several heterogeneous catalysts were screened for this hydrogenation reaction. It was found that iridium and ruthenium on carbon were inactive (entries 6 and 7). In addition, palladium on calcium carbonate and black platinum were also inactive in this case (entries 8 and 9). Palladium on barium sulfate and platinum oxide showed some activity (entries 10 and 11). The most effective catalysts for this reaction were found to be palladium and platinum on charcoal support (entries 12–17). If the results of entries 12 and 13, 14 and 15 are compared, it is obvious that quite a high load of catalyst is needed for full conversion. The explanation for this may be the same as with homogenous catalysts in that some of the active sites of the catalyst are inactivated by the binding of metal to carboxyl groups.

If the results of entries 15 and 17 are compared, it can be found that the hydrogenation of pure hexenuronic



Scheme 2.

Table 1. Hydrogenation tests of hexenuronic acids **1** presented in Schemes 1 and 2^a

Entry	HexA- X_2 : X_3 ^a	Conditions ^b	Ratio 2:3 ^c	Conversion (%) ^d
1	3.7:1	G4-OH(Pd ₄₀) (2.5 mol %), 1 bar, 3 days or (2.5 mol %), 2.6 bar, 24 hours	–	–
2 ^b	3.7:1	[Rh{(R)-binap(SO ₃ Na) ₄ }(H ₂ O) ₂]ClO ₄ (7 mol %), 1 bar, 2 days or (10 mol %), 2.6 bar, 24 hours	–	–
3	3.7:1	Pd[(R)-binap(SO ₃ Na) ₄]Cl ₂ (18 mol %), 1 bar, 4 days ^d or (20 mol %), 2.7 bar, 24 hours	–	–
4	3.7:1	Pt[(R)-binap(SO ₃ Na) ₄]Cl ₂ (20 mol %), 1 bar, 2 days or (19 mol %), 2.7 bar, 24 hours	–	–
5	3.7:1	RuCl ₃ ·xH ₂ O (20 mol %), 1 bar, 2 days	–	–
6	3.7:1	5% Ru/C (51 mol %), 1 bar, 3 days	–	–
7	3.7:1	5% Ir/C (52 mol %), 1 bar, 22 hours	–	–
8	3.7:1	5% Pd/CaCO ₃ (53 mol %), 1 bar, 22 hours	–	–
9	3.7:1	black Pt (43 mol %), 1 bar, 23 hours ^e	–	–
10	3.7:1	PtO ₂ (50 mol %), 1 bar, 20 hours	1:3	5
11	3.7:1	9% Pd/BaSO ₄ (55 mol %), 1 bar, 21 hours	1:2	40
12	3.7:1	10% Pt/C (53 mol %), 1 bar, 22 hours	1:8	100
13	3.7:1	10% Pt/C (19 mol %), 1 bar, 23 hours	1:8	10
14	3.7:1	10% Pd/C (10 mol %), 1 bar, 22 hours	1:1	70
15	3.7:1	10% Pd/C (50 mol %), 1 bar, 2 hours	1:1	100
16	3.7:1	10% Pd/C (50 mol %), 1 bar, 35 mins	1.2:1	100 ^f
17	0:1	10% Pd/C (50 mol %), 1 bar, 2 hours	1:4.7	100

^a Molar ratio of hexenuronic acid xylodiose (HexA- X_2) to xylotriose (HexA- X_3).

^b All of these reactions were done in water solution unless otherwise noted.

^c Determined by ¹H NMR.

^d The yields were between 45–98%. Even excess of catalyst was tried.

^e The same reaction was also tried in different acidic or basic solvent systems at 1 and 3 atm pressure. Even an excess of catalyst was tried.

^f The yield of this reaction was 98%.

acid **1** xylotriose (HexA-X₃) gave more *cis*-hydrogenation product than the mixture of hexenuronic acid **1** attached to xylodiose and xylotriose.

In conclusion, the first hydrogenation of 4-deoxy- β -L-*threo*-hex-4-enopyranosyluronic acid **1** has been accomplished with palladium and platinum on charcoal catalysts. This results in the formation of a mixture of 4-deoxy-L-galacturonic acid **2** and 4-deoxy-D-galacturonic acid **3**. Quite a high load of catalyst is needed for full conversion.

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11. 2D NMR (COSY) of 4-deoxy-L-galacturonic acid **2** (400 MHz, D₂O): δ 5.17 (d, $J=3.6$ Hz), 3.28 (t, $J=6.6$ Hz), 3.80 (dd, $J=11.4, 5.4$ Hz), 2.14 (ddd, $J=7.6, 5.2, 2.4$ Hz), 1.34 (q, $J=12.1$ Hz), 4.42 (d, $J=8.0$ Hz). Also a connection between δ 3.80 and 1.34 was noticed. MS (ES+) m/z 465 of 4-deoxy-galacturonic acid with xylodiose and m/z 597 with xylotriose.
12. 2D NMR (COSY) of 4-deoxy-D-galacturonic acid **3** (400 MHz, D₂O): δ 4.90 (s), 3.37 (d), 3.95 (t), 1.76 (m), 4.07 (dd, $J=11.6, 3.2$ Hz). Other coupling constants are difficult to calculate, because they overlap with xylose peaks.