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Note

Zeolite catalyzed selective deprotection of di- and tri-*O*-isopropylidene sugar acetals

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Dedicated to Professor C. N. Pillai on his 70th birthday

Abstract—H-Beta zeolite, a microporous solid acid, is demonstrated to be an efficient catalyst for the selective deprotection of cyclic as well as acyclic *O*-isopropylidene sugar acetals derived from D-glucose, D-xylose, D-mannose, and D-mannitol in aqueous MeOH at room temperature. A notable observation is the conversion of D-mannitol triacetonide into 1,2:3,4-di-*O*-isopropylidene-D-mannitol (48%) and 3,4-*O*-isopropylidene-D-mannitol (36%) brought about in 6 h by H-beta zeolite and the non-occurrence of any hydrolysis in the case of H-ZSM-5 catalyzed reaction in 24 h under the same conditions.

Keywords: *O*-Isopropylidene acetals; Carbohydrates; Hydrolysis; Zeolites and solid acids

Driven by the growing need for developing synthetic methodologies based on green chemistry, the application of inorganic solid acids, such as zeolites and molecular sieves, as heterogeneous catalysts for solution phase organic transformations is gaining greater attention.[1] The advantages of solid acids over the homogeneous systems include elimination–minimization of (a) hazards in handling of corrosives, (b) difficulty in separation and neutralization, and (c) disposal costs. The following unique characteristics set zeolites apart from other solid acid catalysts: (a) regular pore size and pore architecture, (b) pore widths of molecular dimensions that enable shape or size selective catalysis, and (c) acid–base properties that can be tuned to match substrate reactivity. Thus zeolites offer exciting opportunities for selective transformations of multifunctional molecules such as carbohydrates. Zeolites have been employed, as acid–base catalysts, in carbohydrate chemistry to catalyze reactions such as the formation of *O*-isopropylidene acetals,[2] preparation of 5-hydroxymethylfurfural from fructose and precursors,[3] hydrolysis of di- and polysaccharides,[4] and synthesis of alkyl glucoside surfactants.[5] Zeolite catalyzed cleavage of sugar acetals has, however, been hitherto unexplored.

Protection and deprotection of hydroxyl groups represent important procedures in carbohydrate chemistry.[6] Selectively protected acetals of sugars, such as *O*-isopropylidene derivatives, are useful intermediates for the synthesis of biologically active molecules.[7] Though several homogeneous Lewis/Bronsted catalysts have been employed for the selective deprotection of sugar acetals,[8] reports on the use of solid acids are rather limited and include ion-exchange resin[9] and $FeCl_3/NaHSO_4/HClO_4$ supported on silica gel.[10] As part of our major program on solid acid-catalyzed transformations of carbohydrates and other substrates in the liquid-phase,[11] we report herein on the selective and complete deprotection of several di- and tri-*O*-isopropylidene sugar acetals using H-ZSM-5 and H-beta zeolite as catalysts. Both these zeolites share the common property with their strong Brønsted acid sites. H-ZSM-5 is a 10 ring medium pore zeolite (approximate $d = 5.5$ Å) containing two perpendicularly intersecting

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channel systems, whereas H-beta is a 12 ring large pore zeolite (approximate $d = 7.5$ Å) consisting of two polymorphs A and B, each of which contains straight as well as tortuous channels.[12]

Our initial efforts to bring about the selective deprotection of the diacetonide 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1a**) using H-Y and H-ZSM-5 zeolite in CCl_4–$CHCl_3$ with a stoichiometric amount of water did not afford any product as shown by the TLC analysis of the reaction mixture. Filtration of the catalyst followed by evaporation of the solvent gave back the unreacted starting material. However, extraction of the recovered catalyst with MeOH under refluxing conditions gave a product whose physical and spectral data matched well with those of D-glucose. It was suspected that the adsorbed substrate inside the zeolite pores underwent partial hydrolysis but the product was not desorbing and coming out into the relatively non-polar liquid-phase, thus undergoing complete deprotection to form D-glucose. By remaining inside the pores, D-glucose also prevented catalytic turn over.

Therefore, it was reasoned that the appropriate medium for the selective hydrolysis should be able to dissolve the substrate and also be able to extract the product from zeolite pores when the reaction is in progress. Toward this end, aqueous MeOH was chosen as the medium and selective hydrolysis of **1a** was explored using different solid acids at room temperature (Scheme 1). Following partial/complete conversion after the specified time, the reaction mixture was worked up and the product formed was purified by column chromatography over silica gel. The isolated yield of pure product 1,2-*O*-isopropylidene-α-D-glucofuranose, **2a**, obtained in each of the solid acid catalyzed reactions is shown in Table 1. H-ZSM-5 and H-beta are found to be efficient catalysts in 50% aqueous MeOH medium. A decrease in water content in the medium has led to longer reaction times and lower yield of **2a** in the case of H-ZSM-5 catalyst. However, there was no significant difference in reaction time observed with H-beta zeolite. Even after 48 h of reaction, the conversion in the case of montmorillonite K-10 was rather poor whereas H-Y zeolite turned out to be completely ineffective. H-Beta zeolite catalyzed transformation is much faster as compared to that of H-ZSM-5 as well as that of previously reported heterogeneous Bronsted acid catalysts such as ion-exchange resin[9] and $HClO_4$ supported on silica gel.[10c] Total hydrolysis was observed when the reaction was performed using H-beta zeolite in MeOH–H_2O (1:1) under refluxing conditions for 4 h affording D-glucose in near quantitative yield (94%). The high efficiency of H-beta zeolite compared to other zeolites examined may be due to its greater acid strength coupled with large pore openings and spacious channel intersections.[13]

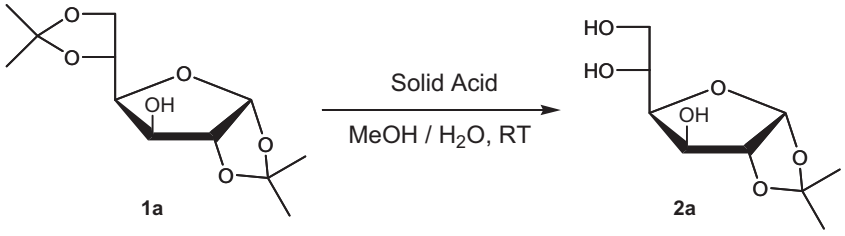
Table 1. Solid acid catalyzed selective cleavage of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (**1**)

Entry	Catalyst	Solvent	Time[a]	Yield of **2**[b] (%)
1	H-ZSM-5	MeOH–H_2O (1:1)	16	92
		MeOH–H_2O (4:1)	48	85
2	H-Beta	MeOH–H_2O (1:1)	2	96
		MeOH–H_2O (9:1)	2	94
		MeOH	4	88
3	Montmorillonite K-10	MeOH–H_2O (1:1)	48	22
4	H-Y	MeOH–H_2O (1:1)	48	—

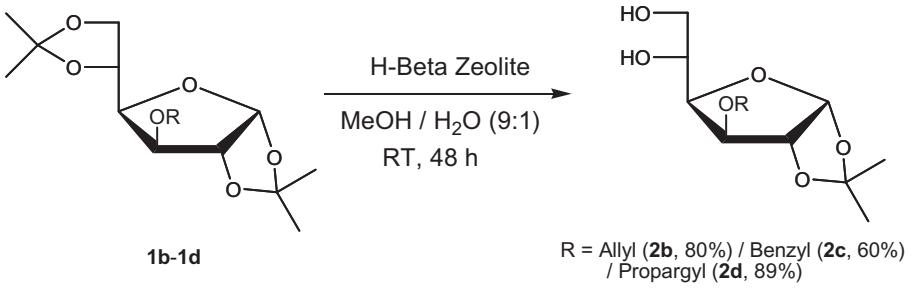
[a] All the reactions were performed at room temperature.
[b] Yield of isolated pure product.

To evaluate the recyclability of the catalyst, H-beta zeolite was filtered from the selective hydrolysis reaction mixture containing **2a**, washed with hot MeOH three times, and dried in the oven at 400 °C. Treatment of **1a** with the first and the second time recycled catalyst in separate reactions afforded **2a** in 97% and 95% yields, respectively. H-Beta zeolite also proved to be effective in bringing about selective deprotection of **2** in the presence of acid-labile protecting groups such as allyl, benzyl, and propargyl (Scheme 2). The yield of the 3-*O*-substituted derivatives **2b**–**d** obtained based on recovery of the starting material was greater than 95% illustrating the stability of these functional groups under the reaction conditions.

In an effort to evaluate the general application of the method, selective hydrolysis of di-*O*-isopropylidene acetals of D-xylose, D-galactose, D-mannose, and D-mannitol (Fig. 1) was examined using H-ZSM-5 and H-beta zeolite in aqueous MeOH at room temperature. The MeOH–H_2O ratio for the reactions was chosen depending on the solubility of the substrates. Whenever possible, a 9:1 ratio of MeOH–H_2O was chosen to facilitate



Scheme 1.



Scheme 2.

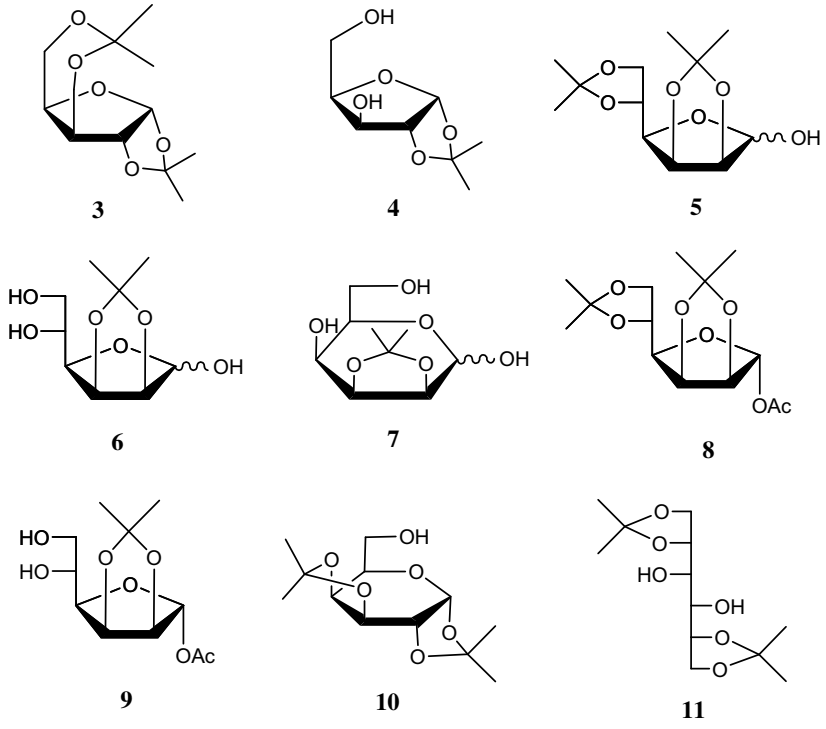


Figure 1.

the easy removal of the medium. 1,2:5,6-Di-*O*-isopropylidene-α-D-xylofuranose (**3**) underwent facile conversion in the presence of both H-ZSM-5 and H-beta zeolite furnishing the monoacetonide 1,2-*O*-isopropylidene-α-D-xylofuranose (**4**) in excellent yields (Table 2, entries 1 and 2). Expectedly, hydrolytic cleavage of the 1,3-dioxane ring in **3** is faster than the 1,3-dioxalane ring of **1a**.[8iiia,14]

Table 2. Zeolite catalyzed cleavage of various di-*O*-isopropylidene sugar derivatives

Entry	Substrate	Catalyst	MeOH–H_2O ratio	Time (h)	Product (yield, %)[a]
1	**3**	H-ZSM-5	1:1	4	**4** (91)
2	**3**	H-Beta	9:1	1	**4** (90)
3	**8**	H-Beta	9:1	8	**9** (97)
4	**10**	H-ZSM-5	1:1	24	—
5	**10**	H-Beta	1:1	24	—
6	**10**	H-Beta	1:1	24	D-Galactose (96)[b]
7	**11**	H-ZSM-5	1:1	48	D-Mannitol (92)
8	**11**	H-Beta	1:1	24	D-Mannitol (96)
9	**11**	H-ZSM-5	1:1	3	D-Mannitol (96)[b]

[a] Yield of isolated pure product.
[b] Reactions were performed at refluxing temperature.

The selective hydrolysis of 2,3:5,6-di-*O*-isopropylidene-D-mannofuranose (**5**) was then examined. Analysis of reaction mixture involving H-ZSM-5 in MeOH–H_2O (1:1) after 60 h and H-beta in MeOH–H_2O (9:1) after 8 h showed on TLC disappearance of **5** and formation of a more polar product compared to **5** in each case, which was identified based on ^1H NMR analysis as a mixture of monoacetonides of D-mannose viz., 2,3-*O*-isopropylidene-D-mannofuranose (**6**) and 2,3-*O*-isopropylidene-D-mannopyranose (**7**). Understandably, the substrate **5** was initially transformed by selective hydrolysis to **6**, which underwent ring modification to form **7** resulting finally in an equilibrium mixture of pyranose and furanose forms. The product complexity problem was solved by protecting the anomeric hydroxyl function in **5** as the acetate and subjecting the same to hydrolysis. Treatment of the monoacetate **8**, 1-*O*-acetyl-2,3:5,6-di-*O*-isopropylidene-D-mannofuranose, with H-beta zeolite in MeOH–H_2O (9:1) at room temperature for 8 h afforded 1-*O*-acetyl-2,3-*O*-isopropylidene-D-mannofuranose (**9**) as the single product in excellent yield (97%).

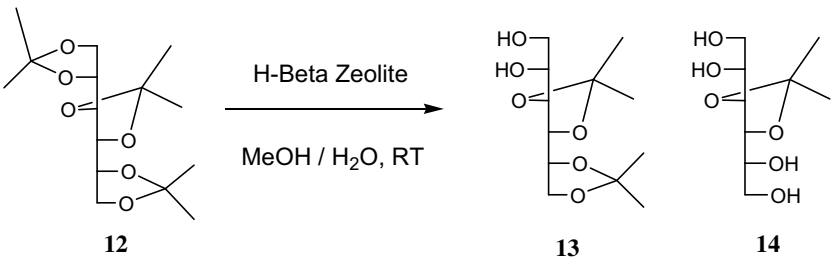
Having found H-ZSM-5 and H-beta zeolite as efficient catalysts for selective deprotection of di-*O*-isopropylidene derivatives derived from furanose systems, their utility for achieving the same with a pyranose system was examined. 1,2:3,4-Di-*O*-isopropylidene-α-D-galactopyranose (**10**) was allowed to react in the presence of H-ZSM-5 or H-beta zeolite in MeOH–H_2O (1:1) at room temperature. The substrate remained unchanged even after 24 h in both cases (entries 4 and 5). However, when the reaction was performed using H-beta zeolite in MeOH–H_2O (1:1) under refluxing conditions for 24 h, cleavage of both acetonide groups occurred affording D-galactose in near quantitative yield (Table 2, entry 6). In the case of acyclic diacetonide, 1,2:5,6-di-*O*-isopropylidene-D-mannitol (**11**), treatment with H-ZSM-5 at room temperature in MeOH–H_2O (1:1) led to hydrolysis, although not selectively, to form D-mannitol in excellent yield (Table 2, entry 7). H-Beta zeolite effected the same transformation in shorter time (Table 2, entry 8). The reaction time for the H-ZSM-5 catalyzed complete hydrolysis was reduced by performing the reaction under refluxing condition (Table 2, entry 9).

Moving forward from di-*O*-isopropylidene acetals to tri-*O*-isopropylidene acetals, the hydrolysis of 1,2:3,4:5,6-tri-*O*-isopropylidene-D-mannitol (**12**) was then explored (Scheme 3). The triacetonide **12** underwent facile hydrolysis in the presence of H-beta zeolite in MeOH–H_2O (9:1) to form the 1,2:3,4-di-*O*-isopropylidene-D-mannitol (**13**) and 3,4-*O*-isopropylidene-D-mannitol (**14**) in 48% and 36% yields, respectively (Table 3). Interestingly, there was no reaction observed when H-ZSM-5 was used under the above conditions (Table 3, entries 2 and 3). The failure of H-ZSM-5 to effect this transformation could be ascribed to its small pore openings, making it difficult for the bulky triacetonide to enter into the pores for catalysis to occur. The reported[15] crystal structure of **12** lends support to this reasoning. The selectively protected 1,2:3,4-di-*O*-isopropylidene acetal (**13**) of D-mannitol was known to be a valuable chiral intermediate for the synthesis of many natural products and pharmaceutical intermediates.[16] The reported procedure[17] for the preparation of **13** from **12** gives lower yields and involves the use of concentrated hydrochloric acid and tedious work-up. This is the first report on the use of a solid acid for selective deprotection of a tri-*O*-alkylidene sugar derivative.

In conclusion, we have developed an efficient heterogeneous catalytic procedure for selective hydrolysis of di- and tri-*O*-isopropylidene sugar acetals at room temperature using the proton form of the commercially available ZSM-5 and beta zeolites. Complete hydrolysis of di-*O*-isopropylidene derivatives has also been demonstrated under refluxing conditions. A notable observation is the conversion of D-mannitol triacetonide into 1,2:3,4-di-*O*-isopropylidene-D-mannitol and 3,4-*O*-isopropylidene-D-mannitol in good yields brought about by H-beta zeolite. The method developed would prove

Table 3. Zeolite catalyzed cleavage of 1,2:3,4:5,6-tri-*O*-isopropylidene-D-mannitol (**12**)

Entry	Catalyst	MeOH–H_2O ratio	Time (h)	Product (yield %)
1	H-Beta	9:1	6	**13** (48) and **14** (36)
2	H-ZSM-5	9:1	24	No reaction
3	H-ZSM-5	1:1	24	No reaction



12 **13** **14**

Scheme 3.

to be very useful in providing efficient and convenient access to several selectively protected sugar acetals that serve as renewable chiral pools for the synthesis of natural products.

1. Experimental

1.1. General

Thin layer chromatography was performed on micro slides coated with silica gel (200–300 mesh) of 0.1 mm thickness. The components on TLC were visualized by spraying with 10% H_2SO_4 in MeOH and heating on a hot plate. Column chromatography was performed by gravity method using silica gel (60–120 mesh) using a mixture of ethyl acetate and hexane. Melting points were determined on a Toshniwal melting point apparatus and are uncorrected. Specific rotations were determined with JASCO-DIP 200 digital polarimeter. IR spectra were recorded on a Shimadzu IR-470 spectrometer. NMR spectra were recorded with JEOL GSX-400 or Bruker AV400 spectrometer using TMS as internal standard. Electrospray ionization mass spectral (ESI-MS) analyses were performed with a Micromass Q-Tof mass spectrometer in the positive ion mode.

1.2. Materials

All sugars used were purchased from Sigma–Aldrich USA or from Pfanstiehl Laboratories Inc. USA and used as such. Montmorillonite K-10 was obtained from Fluka. Beta and ZSM-5 zeolite, obtained from Süd-Chemie India Limited New Delhi, and Y-zeolite (H-β, Si/Al = 101; H-ZSM-5, Si/Al = 454; H-Y, Si/Al = 8.6) were converted to H-form by using standard procedure.[18] All the substrates were prepared according to the reported procedures: 1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (**1a**),[19] 3-*O*-allyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (**1b**),[20] 3-*O*-benzyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (**1c**),[21] 3-*O*-propargyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (**1d**),[22] 1,2:3,5-di-*O*-isopropylidene-D-xylofuranose (**3**),[23] 2,3:5,6-di-*O*-isopropylidene-D-mannose (**5**),[19] 1-*O*-acetyl-2,3:5,6-di-*O*-isopropylidene-α-D-mannofuranose (**8**)[24] 1,2:3,4-di-*O*-isopropylidene-α-D-galactopyranose (**10**),[25] 1,2:5,6-di-*O*-isopropylidene-D-mannitol (**11**),[26] and 1,2:3,4:5,6-tri-*O*-isopropylidene-D-mannitol (**12**).[17]

1.3. Typical procedure for the selective hydrolysis

To a solution of **3** (0.46 g, 2 mmol) in MeOH–H_2O (9:1) (20 mL), H-beta zeolite (0.5 g) was added and stirred at room temperature. TLC analysis of the reaction mixture showed the disappearance of the substrate after 4 h. The catalyst was then filtered through Celite pad and washed with MeOH. The filtrate combined with washings was concentrated under reduced pressure and the residual water was co-evaporated with EtOH–toluene (1:2) under reduced pressure to afford a colorless syrup which on further purification by column chromatography over silica gel using chloroform–MeOH (9:1) gave a pure product **4** (yield 0.34 g, 91%).

1.3.1. 1,2-*O*-Isopropylidene-α-D-glucofuranose (2a). Yield 0.41 g (94%), mp 158–160 °C [lit.[19] 160–161 °C], $[\alpha]_D$ −12.4 (*c* 1.0, H_2O) [lit.[19] −11.4 (H_2O)]; ^{1}H NMR (D_2O) δ 6.02 (d, 1H, $J = 3.4$ Hz, H-1), 4.70 (d, 1H, H-2), 4.32 (d, 1H, H-3), 4.10 (dd, 1H, H-4), 3.92 (m, 1H, H-5), 3.80 (dd, 1H, $J = 12.2$ Hz, 2.9 Hz, H-6), 3.64 (dd, 1H, $J = 12.2$ Hz, 6.3 Hz, H-6′), 1.52 and 1.36 (s each, 2 × 3H, 2 × CH_3); ^{13}C NMR (D_2O) δ 110.9 (s), 102.9 (d, C-1), 82.6 (d, C-2), 78.0 (d, C-4), 71.8 (d, C-3), 66.6 (d, C-5), 61.7 (t, C-6), 23.7, 23.3 (2q, 2 × CH_3).

1.3.2. 3-*O*-Allyl-1,2-*O*-isopropylidene-α-D-glucofuranose (2b). Yield 0.24 g (80%), syrup, $[\alpha]_D$ −37.2 (*c* 1.0, $CHCl_3$) [lit.[27] −30.2 ($CHCl_3$)]; ^{1}H NMR ($CDCl_3$) δ 5.92 (d, 1H, $J = 3.6$ Hz, H-1), 5.98–5.85 (m, 1H, CH_2═CH–), 5.33 and 5.24 (m, each, 2H, CH_2═CH–), 4.58 (d, 1H, H-2), 4.23–4.00 (m, 5H, H-3, H-4, H-5 and –CH_2–), 3.84 (dd, 1H, $J = 3.2$ Hz, 11.6 Hz, H-6a), 3.74 (dd, 1H, $J = 5.6$ Hz, 11.6 Hz, H-6b), 1.49 (s, 3H, CH_3) and 1.32 (s, 3H, CH_3).

1.3.3. 3-*O*-Benzyl-1,2-*O*-isopropylidene-α-D-glucofuranose (2c). Yield 0.19 g (60%), syrup, $[\alpha]_D$ −42.3 (*c* 0.6, $CHCl_3$) [lit.[27] −46.2 ($CHCl_3$)]; ^{1}H NMR ($CDCl_3$) δ 7.41–7.28 (m, 5H, Ph), 5.94 (d, 1H, $J = 3.6$ Hz, H-1), 4.73 and 4.56 (AB q, 2H, –CH_2Ph), 4.63 (d, 1H, $J = 3.6$ Hz, H-2), 4.16–4.07 (m, 2H, H-3 and H-4), 4.03 (m, 1H, H-5), 3.81 (dd,1H, $J = 3.2$ Hz, 11.6 Hz, H-6a), 3.70 (dd, 1H, $J = 5.6$ Hz, 11.6 Hz, H-6b), 1.49 (s, 3H, CH_3) and 1.32 (s, 3H, CH_3).

1.3.4. 3-*O*-Propargyl-1,2-*O*-isopropylidene-α-D-glucofuranose (2d). Yield 0.12 g (89%), syrup, $[\alpha]_D$ −54.6 (*c* 0.6, $CHCl_3$) [lit.[28] −37.7 ($CHCl_3$)]; ^{1}H NMR ($CDCl_3$) δ 5.91 (d, 1H, $J = 3.6$ Hz, H-1), 4.61 (d, 1H, $J = 3.6$ Hz, H-2), 4.38–4.22 (m, 3H, H-3 and –CH_2–), 4.17 (dd, 1H, $J = 3.2$ Hz, 8.4 Hz, 8.4 Hz, H-4), 3.99 (m, 1H, H-5), 3.84 (dd, 1H, $J = 5.6$ Hz, 11.6 Hz, H-6a), 3.74 (dd, 1H, $J = 5.6$ Hz, 11.6 Hz, H-6b), 1.50 (s, 3H, CH_3) and 1.32 (s, 3H, CH_3).

1.3.5. 1,2-*O*-Isopropylidene-α-D-xylofuranose (4). Yield, 0.34 g (91%); $[\alpha]_D$ −18.9 (*c* 1, H_2O) [lit.[29] −20.6 (H_2O)]; ^{1}H NMR (D_2O) δ 6.05 (d, 1H, J = 3.9 Hz, H-1), 4.70 (d, 1H, $J = 3.9$ Hz, H-2), 4.30 (m, 2H, H-3, H-4), 3.88 (dd, 1H, H-5), 3.79 (dd, 1H, H-5′), 1.54, 1.38 (s each, 2 × 3H, 2 × CH_3); ^{13}C NMR (D_2O) δ

111.9 (s), 103.8 (d, C-1), 84.1 (d, C-2), 80.5 (d, C-4), 73.2 (d, C-3), 58.7 (t, C-5), 24.9, 24.5 (2 × q, 2 × CH_3).

1.3.6. 1-*O*-Acetyl-2,3-*O*-isopropylidene-α-D-mannofuranose (9). Yield 0.51 g (97%); $[\alpha]_D$ +70.0 (*c* 4.0, $CHCl_3$); IR (neat) cm^{-1} 3392, 2928, 1702, 1641, 1363, 1251, 1235, 1060, 956, 873, 806; ^1H NMR ($CDCl_3$) δ 6.14 (s, 1H, H-1), 4.90 (dd, 1H, $J = 5.9$ Hz, 3.7 Hz, H-3), 4.69 (d, 1H, $J = 6.0$ Hz, H-2), 4.10 (dd, 1H, $J = 8.3$ Hz, 3.8 Hz, H-4), 4.00 (m, 1H, H-5), 3.84 (dd, 1H, $J = 11.5$ Hz, 3.2 Hz, H-6), 3.70 (dd, 1H, $J = 11.5$ Hz, 5.4 Hz, H-6′), 2.06 (s, 3H, CH_3CO), 1.48, 1.33 (s each, 2 × 3 H, 2 × CH_3); ^{13}C NMR ($CDCl_3$) δ 167.8, 111.4, 98.9 (C-1), 82.9, 79.4, 77.9, 68.0, 62.2, 24.2 (CH_3CO), 22.9, 19.4 (2 × CH_3); HRMS (ESI) calculated for $C_{11}H_{18}O_7Na$ $[M+Na]^+$: 285.0950, found: 285.0958.

1.3.7. 1,2:3,4-Di-O-isopropylidene-D-mannitol (13). Yield 0.25 g (48%); $[\alpha]_D$ +18.8 (*c* 0.9, H_2O) [lit.[30] +5.15 ($CHCl_3$)]; ^1H NMR ($CDCl_3$) δ 4.22 (dd, 1H, $J = 8.3$ Hz, 5.8 Hz, H-1), 4.08 (m, 1H, H-2), 4.03 (dd, 1H, $J = 8.3$ Hz, 4.9 Hz, H-1′), 3.91 (t, 1H, $J = 7.3$ Hz, H-3), 3.82–3.77 (m, 2H), 3.75–3.69 (m, 2H), 1.46 (s, 3H, CH3), 1.38 (s, 3H, CH3), 1.37 (s, 6H, 2 × CH_3); ^{13}C NMR ($CDCl_3$) δ 110.2 (s), 109.6 (s), 80.63 (d, C-4), 80.57 (d, C-3), 76.4 (d, C-2) 72.0 (d, C-5), 67.9 (t, C-1), 63.5 (t, C-6), 26.7, 26.3, 25.0.

1.3.8. 3,4-*O*-Isopropylidene-D-mannitol (14). Yield 0.16 g (36%); mp 86–88 °C [lit.[17] 86–87 °C]; $[\alpha]_D$ +27.6 (*c* 1.1, H_2O) [lit.[31] +29.8 (H_2O)]; ^1H NMR (D_2O) δ 3.90–3.87 (m, 2H), 3.61–3.55 (m, 4H), 3.43–3.38 (m, 2H), 1.23 (s, 6H, $C(CH_3)_2$); ^{13}C NMR (D_2O–DMSO-d_6) δ 109.8 (s), 78.2 (d, C-3 and C-4), 71.8 (d, C-2 and C-5), 62.1 (t, C-1 and C-6), 26.0 (q, 2 × CH_3).

1.4. Typical procedure for the complete hydrolysis

To a solution of **1** (0.52 g, 2 mmol) in MeOH–H_2O (1:1, 20 mL), H-beta zeolite (0.5 g) was added and the reaction mixture was stirred at reflux. Following the complete disappearance of substrate after 4 h, the reaction mixture was worked up as described in Section 1.3 to obtain a colorless solid identified as D-glucose based on comparison of physical and spectral data with those of an authentic sample (yield 0.34 g, 94%).

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.carres.2008.05.006.

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