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Rapid, one pot preparation of D-mannose and D-mannitol from starch: the effect of microwave irradiation and Mo^{VI} catalyst

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ABSTRACT

The effect of microwave irradiation upon starch hydrolysis and simultaneous epimerization of the D-glucose to D-mannose obtained was investigated. An acidic aqueous solution of starch was treated with a catalytic amount of hexavalent molybdenum salt in microwave field and the composition of the reaction mixture was analyzed. Rapid starch hydrolysis and subsequent epimerization provided an equilibrium reaction mixture of D-glucose and D-mannose (2:1) without the formation of any undesirable by-products. The reduction of D-mannose with sodium borohydride yielded D-mannitol in very good yield. Microwave irradiation proved to be an efficient tool for the transformation of starch to mannose over an Mo^{VI} catalyst. This method has the advantages of environmental friendliness, easy operation, good yields and substantial reduction of reaction time.

1. Introduction

The use of renewable resources and the development of environmentally friendly processes for the preparation of various chemical compounds is very important today.[1] Carbohydrates are the most abundant natural organic compounds, mostly present in polymeric forms, and are amongst the most intensively studied precursors with a wide range of properties and applications.[2] Starch is the second most abundant biopolymer in Nature after cellulose. It has higher viability than cellulose because its depolymerization process is easier. Starch, a polysaccharide consisting of D-glucose linked with α-glycosidic linkages, could serve as a sustainable primary resource of carbohydrate molecules for the chemical industry.[3] However, only few purposes have been found so far for raw, native starch. This natural material is often modified by various chemical or enzymatic methods to obtain useful products used in the food and pharmaceutical industries.[4–6]

Considerable effort has been expended to achieve efficient polysaccharide depolymerization and utilization of the monosaccharides obtained as a source for the synthesis of many carbon feedstocks. Nowadays, the synthesis of organic compounds using microwaves attracts research due to short reaction times, high yields and improved selectivity.[7] Microwave reactors produce efficient internal heating by the direct coupling of microwave energy with the molecules (solvents, reagents or catalysts) present in the reaction mixtures. The different applications of microwave irradiation for fast and reproducible syntheses have been thoroughly discussed.[8–10] It is known that the addition of salts to solvents can increase their conductivity and the solution of substance may be heated up much more rapidly than is done by other convective–conductive heating sources such as an oil bath. The presence of ions can frequently enhance the effects of dielectric loss and microwave coupling and could produce superheating.[11–13] The interaction of metal ions with carbohydrates has been extensively studied for a long time.[14,15] Carbohydrate chemistry is currently dealing with the development of efficient methods for the conversion of carbohydrates into more valuable and enantiomerically pure products. One of the significant achievements in this field is the epimerization reaction of aldoses catalyzed by molybdate ions[16–18] known as the Bílik reaction.[19,20] Molybdate ions were investigated as catalyst for the isomerization of various reducing sugars and it has been shown that in a microwave field, the transformation proceeds very efficiently. This approach was thus found to be an effective way for the isomerization of a carbohydrate carbon skeleton with high stereospecificity. This procedure led to the efficient preparation of aldoses,[21] 2-*C*-(hydroxymethyl)-branched aldoses, ketoses,[22] (1→6)-linked disaccharides[23] but it is also effective in the case of aldoses bearing nitrogen in the branch.[24]

Recent research has shown that starch strongly interacts with microwave irradiation and has different properties compared to conventionally heated reactions. Several papers have reported the hydrolysis of starch in microwave field.[13,25–28] Since one of the important features of current chemistry methods is the effective preparation of compounds from naturally-occurring sources, we have undertaken to find even more efficient method to convert starch not only to glucose but directly to other important compounds. We examined the properties of molybdate salts to act as

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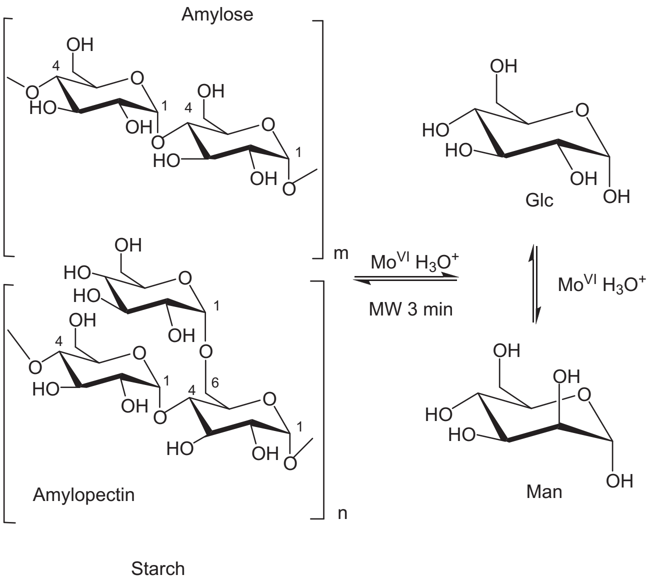
convenient ions to increase the efficiency of heating under conditions of microwave irradiation together with their catalytic properties to improve the process of starch hydrolysis and simultaneous epimerization of obtained D-glucose to commercially interesting D-mannose.

2. Results and discussion

To develop an efficient, rapid and environmentally friendly procedure for the production of commercially interesting D-mannose from native starch, we explored the use of microwave irradiation in combination with a hexavalent molybdenum catalyst. Molybdate ions act as a powerful catalyst for the isomerization of reducing sugars and have a number of unique features.[29–31] To access the potential of Mo^{VI} ions for the starch transformation a series of preliminary experiments were carried out by irradiating mixtures of starch in aqueous solutions of hydrochloric acid containing molybdate salts in a range of concentrations in a microwave field. A survey of reaction conditions was undertaken for this transformation. Based on a broad variable set in terms of acid concentration, amount of catalyst, reaction time, and microwave power, the influence of the different variables could be evaluated to identify correlations between the reaction conditions and starch conversion as well as product distribution.

In the first experiment, five aqueous solutions of hydrochloric acid (0.1; 0.25; 0.5; 0.75 and 1.0 M) were tested for the hydrolysis of starch samples in a microwave field. The depolymerization of 1,4-α- and 1,6-α-glycosidic linkages of starch to D-glucose worked smoothly in 0.25 M hydrochloric acid in a microwave field. The cleavage of α-glycosidic linkages was achieved via the addition of water catalyzed by acid. It was observed that starch hydrolysis is predominantly determined by acid concentration independent of the starch source used. As expected, faster conversion of starch to D-glucose can be reached in the reaction performed using higher concentrations of acid. Our investigations focused on the development of a catalytic system that would improve starch hydrolysis with subsequent epimerization of D-glucose to D-mannose. Hence in the following experiments, the effects of molybdic acid salts on hydrolysis were examined. Comprehensive investigations on the combined hydrolysis and isomerization reactions in one step were carried out using catalytic amounts of sodium molybdate and dilute hydrochloric acid. It was found that a 0.5% solution of sodium molybdate was a sufficiently high concentration of this catalyst and led to very good conversion to products. It should be noted that increasing the amount of catalyst did not have a significant effect on the product composition. The effect of microwave irradiation on conversion, selectivity and product distribution was examined using a multimode microwave reactor consisting of a continuous focused microwave power delivery system with operator-selectable power. It was observed that the microwave power significantly influences the course of the reaction. The best results were obtained by performing the reaction at 200 W of microwave power for 3–5 min.

In the optimized reaction conditions, a 5% solution of starch in 0.25 M hydrochloric acid with a catalytic amount of sodium molybdate was exposed to microwave irradiation in a sealed vessel for different time periods. Homogenous blue solutions were obtained, indicating the completion of the complex formation. Selected reaction conditions led to complete depolymerization of starch and high conversion by means of D-glucose and D-mannose content (2:1). It was observed that the transformation occurs with full selectivity and an equilibrium reaction mixture was reached within 3 min. The reaction scheme of the combined starch hydrolysis and simultaneous epimerization reaction of obtained D-glucose to D-mannose is illustrated in Scheme 1.



Scheme 1. The reaction scheme of starch hydrolysis and simultaneous epimerization of the obtained D-glucose to D-mannose in a microwave field.

The effects of starch sources on the yields of D-mannose were compared using three different starches in subsequent experiments: potato starch, corn starch and rice starch. A solution of each starch in 0.25 M hydrochloric acid with a catalytic amount of sodium molybdate was exposed to microwave irradiation under previously optimized conditions. The ratio of the sugars present in the equilibrium reaction mixture with respect to the production of D-mannose was determined by ^1H NMR spectroscopy. Fractionization of the reaction mixture by column chromatography afforded D-glucose (62–65%) and D-mannose (30–33%). The efficiency of the method was also demonstrated in the semi-preparative scale. The transformation occurs in 3 min reaching comparable final concentrations as listed in Table 1. Regarding the influence of the Mo^{VI} catalyst in acidic aqueous solution in combination with microwave power, minor differences of higher overall conversion to glucose/mannose among three different starches tested seem insignificant. Starch hydrolysis is predominantly determined by acid concentration but the simultaneous mutual interconversion of D-glucose and D-mannose is governed by a highly stereospecific isomerization reaction that is catalyzed only by molybdate ions.

The microwave heated samples of starch were compared with samples prepared by conduction heating (90 °C, oil bath). Starch hydrolysis using the same reaction conditions (0.5% $Na_2MoO_4 \cdot 2H_2O$ in 0.25 M HCl) proceeded very slowly. Under conventional conditions the equilibrium reaction mixtures were obtained after 35–40 h of heating. The analysis of the ^1H NMR spectra indicated that the starch was completely hydrolyzed and converted to the equilibrium mixture (3:1) of glucose and mannose. The formation of D-mannose started in about 6 h and the maximum was reached in about 35–40 h. The final equilibrium mixture was comparable to that found in previous studies of D-Glc/D-Man epimerization.[16,17] Different reaction kinetics and thermodynamics under conventional conditions, compared to microwave conditions, were seen in the large differences in both time-course and the composition of reaction mixture during reaction. After 10 h of heating, the ratio of Glc/Man was 5:1 while the equilibrium mixture of Glc/Man (3:1) was reached after 35 h of heating. The composition of the reaction mixture in terms of starch, D-glucose and D-mannose content as a function of time is depicted in Figure 1.

Different reaction kinetics and thermodynamics were observed using microwave heating. Starch hydrolysis and molybdic

Table 1
Comparison of microwave and conduction-heated samples of the combined starch hydrolysis and simultaneous epimerization reaction of obtained D-glucose to D-mannose

Starch source	MW field		Conventional (%)		Heating	
	Time (min)	Starch/Glc/Man (%)	Time (h)	Starch/Glc/Man (%)	Time (h)	Starch/Glc/Man (%)
Potato starch	3	0/65/33	10	52/35/7	40	0/73/24
Corn starch	3	0/62/30	10	56/32/6	40	0/74/24
Rice starch	3	0/63/31	10	55/31/6	40	0/73/22

Both partial and full conversions are shown for conventional heating to demonstrate vast differences between microwave and conventional approaches in reaction kinetics and amounts of mannose formations.

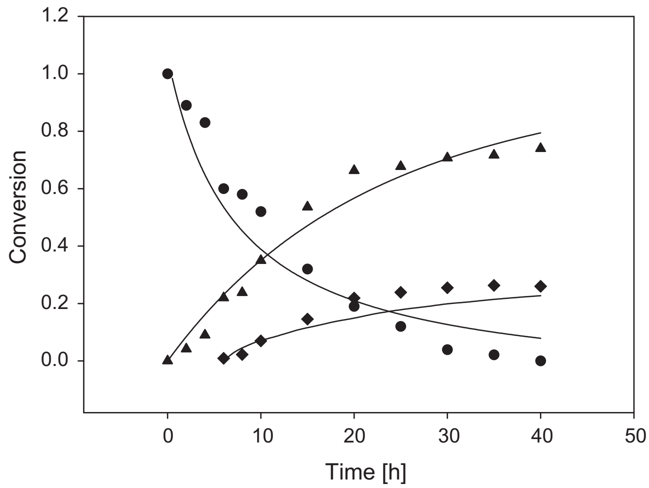


Figure 1. Conversion of potato starch (●) to D-glucose (▲) and D-mannose (♦) as a function of time under conventional, oil-bath heating. The formation of D-mannose starts at approximately 6 h after starch hydrolysis to D-glucose.

acid-catalyzed isomerization reached thermodynamic equilibrium after 3 min under identical reaction conditions (concentrations, temperature) as used for conventional heating (Fig. 2). As seen in Table 1, the studied conversion of starch to the mixture of Glc/Man was dramatically faster. Furthermore, the ratio of Glc/Man was considerably higher (2:1) than that obtained under the classical conditions (5:1 after 10 h; 3:1 after 35 h). Table 1 summarizes all of the data obtained for starch samples heated by using conduction or microwave energy sources. Microwave-induced hydrolysis in the presence of sodium molybdate as a catalyst afforded similar yields of glucose/mannose in all three starch samples tested. There were only minor differences in the composition of the reaction mixtures of various starches. It should be noted that only a catalytic amount of sodium molybdate is very effective and that a higher amount of catalyst does not significantly change the conversion to the product (1–2%).

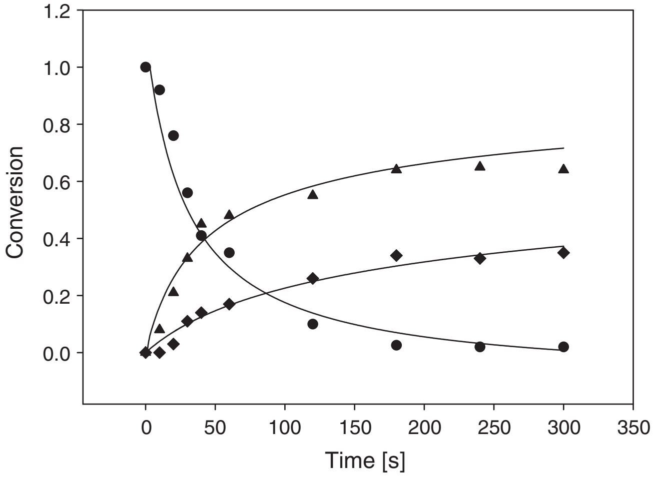


Figure 2. Conversion of potato starch (●) to D-glucose (▲) and D-mannose (♦) as a function of time in a microwave field.

The rearrangement of the obtained D-glucose to D-mannose was accomplished after acid hydrolysis of starch in a microwave field using Mo^{VI} ions as a catalytically active species. In this respect, D-glucose isomerization is a crucial step in the efficient production of D-mannose as a valuable chemical product. The mechanism of this transformation is based on the fact that in the presence of molybdate ions, the hydroxyl groups of the free glucose unit coordinate with the dimolybdate anion and the creation of catalytically active complexes leads to isomerization of D-glucose to D-mannose through high rearrangements of the carbohydrate carbon skeleton.[20,21]

It is important to note that different conversions to products could be obtained in a microwave field as a function of time. The comparison of the results clearly shows that microwave irradiation markedly accelerated the isomerization process (by two orders of magnitude over conventional heating) and that the microwave field also caused differences in the equilibration of the reaction mixtures. Microwave irradiation as a non-conventional energy source thus has a strong influence upon the kinetics and thermodynamics of this reaction. The data obtained suggest that the synergistic coordination ability of the catalyst used under the given reaction conditions enables simultaneous efficient starch depolymerization and the formation of a new compound D-mannose in a single step. Thus, unlike conventional heating, D-mannose is formed virtually simultaneously with D-glucose using microwave radiation. This approach opens up the way for the preparation of many interesting sugar derivatives. It should also be noted that the presence of molybdate ions improves the efficiency of energy absorption from the microwave source and thus the reaction proceeds faster compared to that without the presence of these ions. The Mo^{VI} ions thus perform a double role in the present reaction: the first role is the improvement of the dielectric properties of the solution, leading to high energy transfer to solution from a microwave source; secondly, Mo^{VI} acts as an efficient catalyst that enables the stereospecific conversion of glucose to mannose. These twofold roles of molybdate ions make Mo^{VI} a unique catalyst for the isomerization reactions of carbohydrate molecules.

The main purpose of this study was the development of a practical method for starch hydrolysis with subsequent efficient production of D-mannose and D-mannitol. Both of these products are widely used in the food and pharmaceutical industry.[32–34] The reduction of D-mannose with sodium borohydride leads to D-mannitol in a good yield (78%), hence the production of pure D-mannose is needed in significant amounts. At present, D-mannitol is mainly produced by the reduction of D-fructose from less-expensive glucose–fructose syrups which leads to a mixture of D-mannitol and D-sorbitol (1:1).[35–37] Mixtures of mannitol and sorbitol are also produced enzymatically from fructose with different microorganisms.[38,39] The main problem is that D-mannitol is difficult to separate from its stereoisomer D-sorbitol. Compared to enzymatic production, chemical catalysis employing inexpensive inorganic materials for the isomerization of reducing sugars could offer attractive advantages. Utilizing an efficient catalytic system and water as the solvent has many advantages as this approach is environmentally friendly and inexpensive. Moreover, carbohydrates as water-soluble polar molecules, with high dielectric losses, are suitable chemical systems for microwave irradiation. They could be modified by this approach without the need for protection and deprotection steps. Furthermore, the high demands in activation energy of the isomerization process can be completed in a very short reaction time, which makes aqueous catalysis more efficient. The application of this methodology provides an attractive aspect to the field of microwave-assisted metal-catalyzed reactions in aqueous media.

3. Conclusion

We have developed a direct and convenient microwave assisted one-pot protocol for the preparation of D-mannose from native starch by a simple chemical process. Microwave irradiation in combination with a catalytic amount of molybdate ions proved to be an efficient method for the hydrolysis of starch and isomerization of the obtained D-glucose to D-mannose. The nature of heating had a great impact on this transformation. The rate of starch hydrolysis considerably increased under microwave irradiation. In addition, the conversion of glucose to mannose in the subsequent isomerization step was much higher compared to conventional heating. The short reaction times, good conversions in combination with the easy performance and work-up make this method attractive and also applicable on a semi-preparative scale. In conclusion, we would like to point out that the application of Mo^{VI} salts and microwave power for depolymerization of starch leads to its complete hydrolysis and high conversion by means of D-glucose and D-mannose content.

4. Experimental

4.1. General methods

All starches used were purchased from commercial suppliers. Microwave reactions were performed in a multimode microwave reactor CEM Discover consisting of a continuous focused microwave power delivery system with operator-selectable power from 0 to 300 W; microwave frequency source of 2.45 GHz. The reactions were performed in sealed glass tubes and were stirred magnetically. Conversions and the purities of the products were determined by NMR spectroscopy. High-resolution NMR spectra were recorded in a 5 mm cryoprobe on Varian 600 VNMRS spectrometer. The experiments were carried out at 25 °C in D_2O. The proton and carbon chemical shifts were referenced to external TSP. One-dimensional ^1H and ^{13}C NMR spectra as well as two-dimensional COSY and HSQC were used to determine ^1H and ^{13}C chemical shifts.

Optical rotations were determined at 20 °C with an automatic polarimeter Perkin–Elmer Model 141 using a 10 cm, 1-ml cell. Melting points were measured on a Kofler hotstage microscope. Separations of the free sugars were accomplished by column chromatography on Dowex 50W X8 resin (Sigma–Aldrich) in the Ba^{2+} form (200–400 mesh). Paper chromatography was performed by the descending method on the Whatman No. 1 paper using ethyl acetate–pyridine–water (8:2:1) as the mobile phase. The chromatograms were made visible by means of alkaline silver nitrate. All chemicals were reagent grade and used without further purification.

4.2. Hydrolysis of starch with sodium molybdate under microwave irradiation

Starch (500 mg) was dissolved in 0.25 M HCl (10 ml) and $Na_2MoO_4{\cdot}2H_2O$ (50 mg) was added to obtain a stock solution. The sealed tubes (1 ml) were exposed to microwave irradiation 200 W for different lengths of time (10 s–5 min). Samples were treated with Amberlite IRA-400 in the HCO_3^- form to remove the catalyst. The reaction mixtures were analyzed by NMR spectroscopy measurements and the ratio of starch/glucose/mannose was determined by integration of selected resonances in the ^1H NMR spectra.

4.3. Hydrolysis of starch with sodium molybdate with conventional heating

Starch (200 mg) was dissolved in 0.25 M HCl (4 ml) and $Na_2MoO_4{\cdot}2H_2O$ (20 mg) was added. The tube was sealed and heated in an oil-bath at 90–95 °C for 40 h. Samples (0.3 ml) were taken at selected intervals, and treated with Amberlite IRA-400 in the HCO_3^- form to remove the catalyst. The reaction mixture was analyzed by NMR spectroscopy measurements and the ratio of starch/glucose/mannose was determined by integration of selected resonances in the ^1H NMR spectra.

4.4. Typical procedure for starch hydrolysis under microwave conditions on a semi-preparative scale

Potato starch (500 mg) was dissolved in 0.25 M HCl (10 ml) and $Na_2MoO_4{\cdot}2H_2O$ (50 mg) was added. The sealed tube was exposed to microwave irradiation for 3 min. The reaction mixture was also treated batch-wise with an excess of the cation/anion ion-exchange resin, filtered off, washed with water and the combined filtrates were evaporated. The syrupy residue was fractionated by column chromatography on Dowex 50W X8 (200–400 mesh) in Ba^{2+} form with water as eluent. Fractionization of the syrupy residue afforded D-glucose (0.325 g, 65%) and D-mannose (0.165 g, 33%).

4.5. Reduction of D-mannose to D-mannitol

To a solution of D-mannose (1.0 g) in water (15 ml) was added an aqueous solution of sodium borohydride (0.2 g in 5 ml H_2O). The reaction mixture was kept at room temperature for 2 h. When the reduction was complete the reaction mixture was acidified with a drop of acetic acid, deionized with cation/anion ion-exchange resin and evaporated to dryness. Crystallization from methanol afforded D-mannitol (780 mg; 78%). Mp 165–166 °C; $[\alpha]_D = +23.7 \rightarrow +24.5$ (c 10, $Na_2B_4O_7$), 24 h, which was in accordance with the literature.[40]

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