

Design for Carbohydrate Synthesis: Transformation, Cyclization and Separation of β -D-Glucofuranose and β -D-Glucopyranose by Intercalated Process between Green Catalyst Called Maghnite-H⁺ (Algerian MMT) and D-glucose under Microwave Irradiation

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Abstract: Glucose exists in various forms in solution. At any given time, glucose is present in a 6-membered ring (pyranose) and 5-membered ring (furanose), this second can also be important in biologically domaine. Glucofuranose and glucopyranose isomers could be efficiently synthesized using small amount of maghnite-H⁺ (clay fin 2 % wt) in alkali medium under microwave irradiation. A representative microwave synthesized of glucose isomers was characterized using Fourier Transform Infrared Spectroscopy. Our present investigation showed that the different forms of glucose such as glucofuranose and glucopyranose newly synthesized with green catalyst called maghnite-H⁺(Algerian MMT) in aqueous medium are many more clear in chemicals properties and yield than these synthesized by enzymatic way . Under microwave conditions oxygen removal from the reaction vessel was not required and the products was obtained in high yield using very small amount of clay.

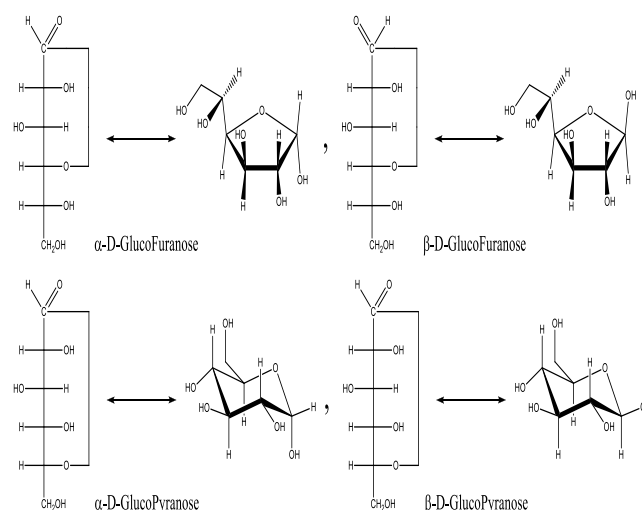
Keywords: *glucofuranose , glucopyranose , monosaccharide , transformation ,isomerization, maghnite-H⁺, MEB*

1 Introduction

Monosaccharides are the simplest form of carbohydrates [1]. They consist of one sugar and are usually colorless [2], water-soluble [3], crystalline solids [4]. Some monosaccharides have a sweet taste [5]. This interest came primarily from the medicinal chemistry community [6], as these new routes often provided access to unnatural sugars. In addition, the synthesis of monosaccharides, and in particular hexoses has served as a challenge and a measuring stick to the synthetic organic community [7].

Most monosaccharides form cyclic structures, which predominate in aqueous solution [8], by forming hemiacetals or hemiketals (depending on whether they are aldoses or ketoses) between an alcohol and the carbonyl group of the same sugars. Glucose, for example, readily forms a hemiacetal linkage between its carbon-1 and the hydroxyl group of its carbon-5 [9]. Since such a reaction introduces an additional stereogenic center, two anomers are formed (α -isomer and β -isomer) from each distinct straight-chain monosaccharide [10]. The interconversion between these two forms is called mutarotation (scheme.1)

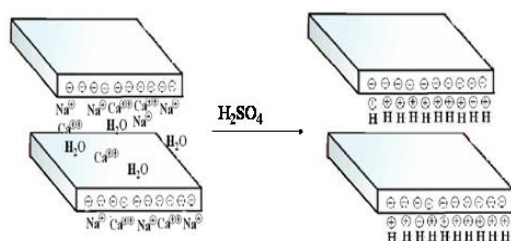
[11].



Scheme 1. Mutarotation form of β -D-glucopyranose and β -D-glucofuranose.

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The clay, which has been used as catalyst [12], is supplied by a local company known as ENOF Maghnia (Western of Algeria). Its active chemical form is given in (scheme 2). The greatest proton saturation of the <2 mm fractions of clay were obtained by first saturating with Na⁺ ions using 1M NaCl solution, then the protonated forms of montmorillonite (Mag-H⁺) were prepared by shaking the clay in a solution of sulfuric acid 0.25M until saturation was achieved (normally after 2 days at room temperature). The cation-exchanged clay was then recovered by filtration, and again suspended in deionized water. This process was repeated until no sulfate ions were indicated present in the filtrate using BaCl₂. The Mag-H⁺ was then isolated by filtration, dried at 105 °C and then finally ground. The cation exchange capacity (CEC) and surface area of the clay was found to be 84 mEq (100 g)⁻¹ of dried clay and 786 m².g⁻¹ respectively [13].



Scheme 2. Activated form of maghnite under sulfuric acid (H₂SO₄, 0.25M)

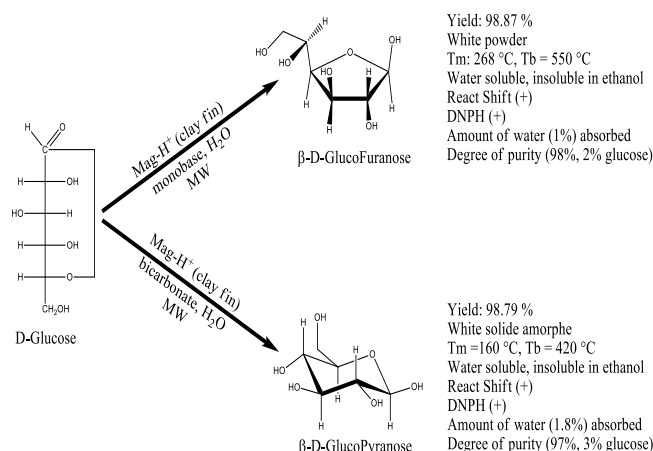
2 Experimental

2.1 Materials

The clay, which has been used as catalyst called (Maghnite-H⁺), is supplied by a local company known as ENOF Maghnia (Western of Algeria). KOH, NaOH, Na₂CO₃, KHCO₃ and K₂CO₃ were obtained from Sigma Aldrich and dried under vacuum at 100°C for 2 minutes to remove water from the crystal.

2.2 Experimental condition

In a flask 250 ml containing D-glucose, we added 0.016 mol of KOH, 50 ml of water and 2 % of Mag-H⁺ (clay fin) previously well dried for 10 minutes in the oven at 120 °C, allowed mixture for 10 minutes at 410 °C. At the end of the reaction, the mixture is filtered, and same time washed with a solvent to recover the catalyst. The residual product (white powder) named β-D-glucopyranose. The same procedure for β-D-glucopyranose, changing just mono base by bicarbonate under the same conditions (scheme 3). The residual β-D-glucopyranose its white solid amorphous.



Scheme 3. Chemical processes for synthesis of β-D-glucopyranose and β-D-glucopyranose catalyzed by Maghnite-H⁺ (clay fin) under microwave irradiation.

3 Results and Discussion

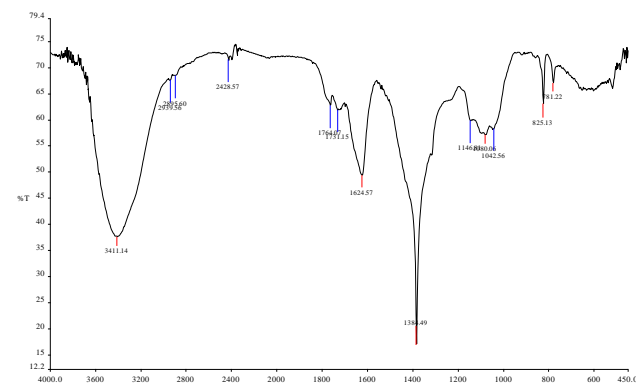


Fig 1. FT-IR spectra of β-D-glucopyranose obtained by the intercalated method between D-glucose and Maghnite-H⁺ (white powder).

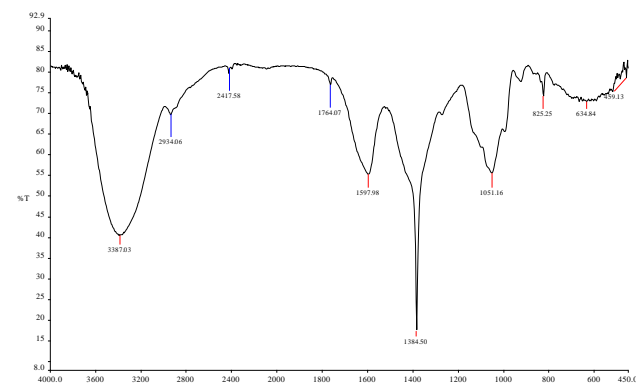


Fig 2. FT-IR spectra of β-D-glucopyranose obtained by the intercalated method between D-glucose and Maghnite-H⁺ (white solid amorphous).

Infrared spectroscopy is a spectroscopy of absorption. When radiation passes through a molecule is observed for certain wavelengths corresponding to absorption frequencies of vibration characteristics of different

chemical bonds [14]. The infrared absorption is a range of spectroscopic techniques to access the modes of vibration of a molecule. These vibration modes involve the internal coordinates of the molecule that is to say the linkages, the valence angles, movements out of the plane and the torsion angles between atoms of the molecule.

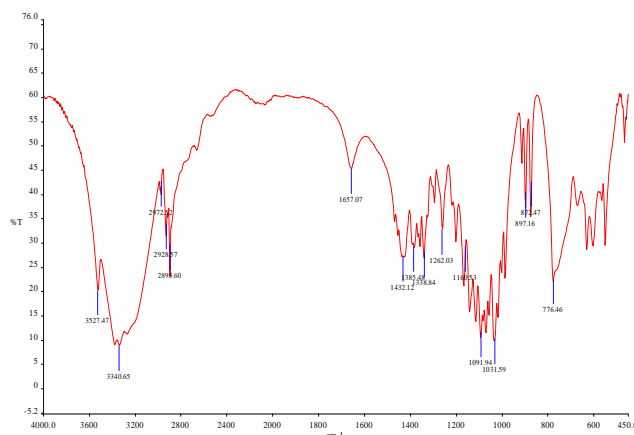


Fig 3. FT-IR spectra of D-glucose (white powder).

The FTIR spectrum shows in figure (1.2), confirms the structure of the D-glucofuranose and D-glucopyranose materials. While the C=O from the carbonyl group shows a weak absorption band at (1764.47cm^{-1} , 1731.15cm^{-1} , 1764.07cm^{-1}), the signal corresponding to vas C-O bond overlaps with the acetal bands that appear around (1146.81cm^{-1} , 1160.53cm^{-1} , 1156.31cm^{-1}) in all mentioned compounds. The broad peak from (3411.14cm^{-1} , 3387.03cm^{-1} , 3340.65cm^{-1}) confirms the generated OH, while the signal at (1624.57cm^{-1} , 1595.98cm^{-1} , 1657.07cm^{-1}) is characteristic of the OH bond from the water absorbed [15].

Area 4000-2450 cm^{-1}

In the high frequency area, we first find the valence of patterns OH group of the group COH observed between 3578 and 3398cm^{-1} . These are virtually the CH stretching mode pure. The CH stretching mode is observed between 3200 and 2800cm^{-1} . These rays are more intense in Infra red spectroscopy, this is found in the majority of saccharide. The modes of symmetric and antisymmetric stretching are located in this region [16].

Area 1900-1200 cm^{-1}

In this area, we see that the bands are of medium intensity and very close together. The modes are coupled and involve different deformations group CH_2OH and also the angular deformation type C-C-H, O-C-H, H-C-H and C-O-H. The methylene groups of the shear modes are in good agreement with literature [17]. Several closely spaced bands of medium intensity were observed between 1600 and 1200cm^{-1} ; these patterns are due to angular deformities C-C-H types O-C-H, C-O-H and coupled with each other and with other modes such as CO and CC

elongation [18,19].

Area 1200-900 cm^{-1}

This area is, in general, very difficult to adjust because of the couplings between the frequencies corresponding to the C-C bonds and C-O endo and exo-cyclic deformations and C-O-H, H-C-O, H-C-H and H-C-C [20]. The frequencies at 1253 and 1240cm^{-1} are attributed to stretching modes C-O. The distribution of potential energy obtained in this region is also according to the work done previously for the disaccharide [21, 22].

Area 900-700 cm^{-1}

This area is called the anomeric region Tulchinsky et col [23], it contains several types of strongly coupled vibrations: deformations of groups C-O-C and C-C-O, pulled and twist of C-C and C-O [24].

Area 700-200 cm^{-1}

In this part of the spectrum are mainly angular deformities C-C-C, C-C-O, O-C-O and C-O-C. This region is characteristic of each saccharide. [25].

The MEB is an important technique that reveals the morphology and the surface of the particles. The MEB utilizes a focused beam of high energy electrons that systematically scans across the surface of the specimen. The solid specimens interact with the electron beam and produce a large number signals at or near the specimen surface [26]. These interactions include lower energy electrons, termed secondary electrons that are generated by knocking-out of weakly bound electrons of the outer electron shells of atoms. Due to their low energy they are from the uppermost nanometers from the surface and thus form the surface characteristics of the sample. The morphology of the composite (D-glucose, D-glucopyranose and D-glucofuranose) were examined with MEB. Fig.4.5.6 illustrates a view of the microstructure of materials. The particles are mechanically interlocked.

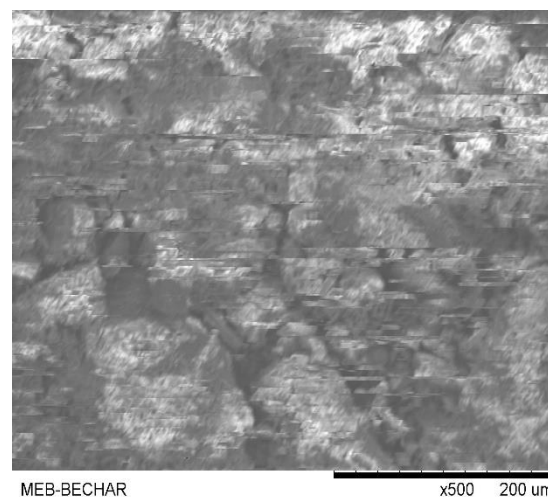


Fig 4. MEB images of β -D-glucofuranose

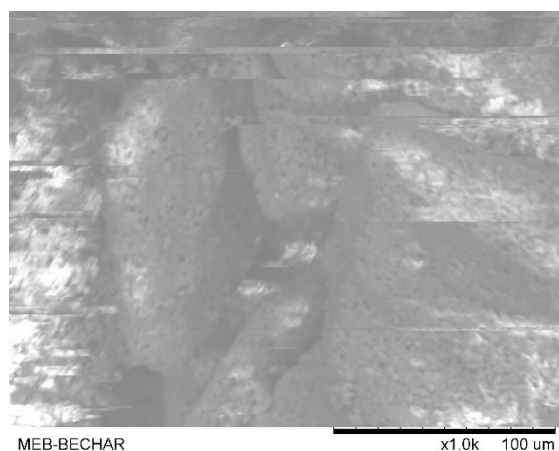


Fig 5. MEB images of β -D-glucopyranose

Particles (white powder) with or without 2% of Mag-H⁺. Particles (white solid amorphous) with or without 2% of Mag-H⁺.

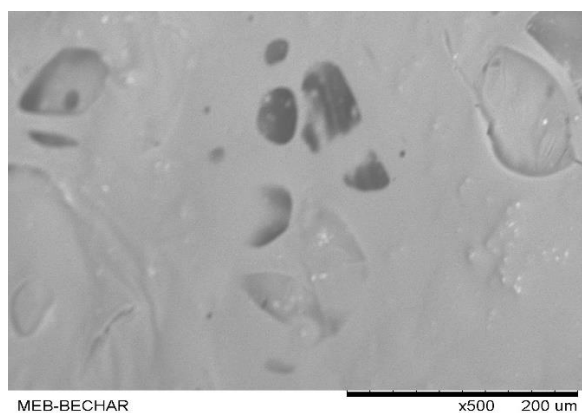


Fig 6. MEB images of D-glucose anhydrous (white powder) particles.

3.1 Kinetics studies

3.2 Effect of amount of catalyst

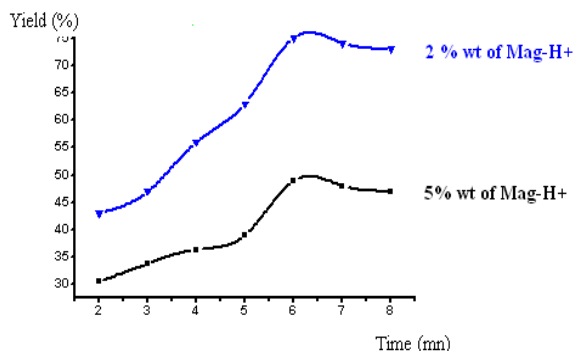


Fig 7. Effect of catalyst (Mag-H⁺ wt 2% and 5%) in the yield of reaction.

Figure 4. Shows the yield of glucofuranose versus time for the reaction of D-glucose using H⁺-MMT as catalyst. As

the figure shows that at the end of 4mn, reaction takes place quickly and reaching a best yield of 83% at the end of 5 mn and in the presence of 2% of H⁺-MMT at 500°C, after this time The reaction slows down gradually and the yield becomes almost constant; this is probably the result of an increase in the medium viscosity. The same phenomenon was observed for the glucopyranose and here we are much optimistic of our catalyst because it is stable in a wide range of temperature and does not change its catalytic and thermal behavior [27].

3.3 Effect of temperature

Using D-glucofuranose and 2 % (Mag-H⁺). The reaction was carried out at different temperatures 10, 100, 165, 210 and 420°C and the effect of temperature was studied. In the absence of H⁺-MMT no reaction could be detected. Figure 5 show that reaction temperature has much influence on the yield of D-glucofuranose. The yield increased with the temperature rising from 100 to 420°C and reached a high yield of 83% at 420°C [28]. This is because increasing the temperature causes an increase in the rate of chain transfer reaction (inter and intramolecular). The same phenomenon was observed for the glucopyranose.

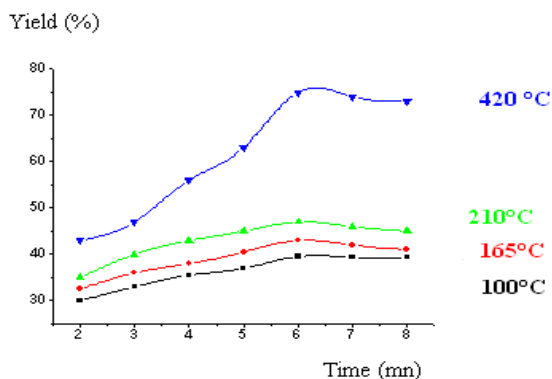


Fig 8. Effect of the temperature in the yield of reaction.

4 Conclusion

Our critically summarizes the applied method for the synthesis, transformation and separation of glucofuranose and glucopyranose by chemical method under effect of green catalyst support called Maghnite-H⁺ (Algerian MMT). These new routes permit the synthesis of rare monosaccharides that are frequently employed in natural products synthesis and also used in pharmaceutical products. The established experimental procedures are provided to illustrate the potential of the synthetic transformation. The reaction proceeds smoothly, and a simple filtration is sufficient to recover the catalyst; the structure of product isomers were confirmed by IR. Herein, we proposed de novo green catalyst to synthesis of carbohydrates, with application to medicinal chemistry studies.

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