Synthesis of Furan Derivatives Polyhydroxylated Chain from the Nuclei of Dates

H. El Mahdi, Z. Abkhar, M.Taourirte, Y.Bachara

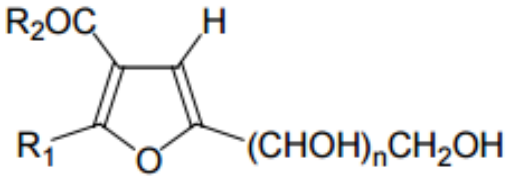
Abstract— This work is part of the valorization of hemicellulose through their transformations into furan derivatives in polyhydroxylated chain that possesses different applications inpolymeres chemistry.The first part focuses on the extraction of hemicelluloses fromthenuclei of dates,a waste abundant generated by the industrial transformations of dates (pastedates, jam ...). Then their hydrolysis in order to obtain pentoses and hexoses.

The originality of the method of extraction of the hemicelluloses in our study, is the first time use of calcium chloride instead of zinc chloride widely used in the presence of acetic acid. Those fresh conditions allow the simultaneous obtaining of lignin and hemicelluloses, making the process economically interesting.

The second part is dedicated to the condensation of mononosaccharides contained in the hydrolyzate with an enolizable compound (ethyl acetoacetate) in the presence of calcium chloride as catalyst to give furan polyols polyhydroxylated chain. The products obtained are identified by the 1 H NMR,and13CNMR

I. INTRODUCTION

Hemicellulose, one of the major constituents of the plant material, are polysaccharides (xylan, glucomannan, galactoglucomanannes, etc ....) which have different applications in various fields: medicine, food, cosmetics and pharmacy. Given the richness of hemicellulose in pentose and hexose, they are a very interesting material for sugar chemistry. Various studies have noted the synthesis of furfural and hydroxymethylfurfural [1, 2] from pentoses and hexoses from hemicellulose. These two compounds are precursors for a wide range of furan monomers used as source of materials. Currently, the most important application of these furan derivatives is the synthesis of resins of furfuryl alcohol [3] used in the cores of foundries and as a coating resistant to high temperatures. Our work is part of the valorization of pentoses and hexoses present in hemicellulose (agricultural waste from agricultural or industrial transformation) by their furan products transformations, different from those mentioned above. These products have in addition to the furan ring, which gives the material a high thermal resistance, a polyhydroxylated chain (Fig. 1) that gives polymers a higher molecular weight, increasing their performance.



$R_1 = CH_3$; $R_2 = OC_2H_5$, CH_3

n=3 for pentoses ; n=4 for hexoses

Fig. 1: Polyol furan (general form)

The action of the polyhydroxylated chain furan polyol from glucose on isocyanate has led to very interesting polyurethanes characters [4] such as the rigidity and the non-flammability. Conclusive tests have also been performed on the furane polyol from xylose [4]. The ester functional group present on the ring can be converted to alcohol, aldehyde, amine or isosyanate to give other monomers [5]. The cycloaddition of furan derivatives with several different dienophiles has been extensively studied [5, 6].

This way can lead to obtain either polycondensates or modify polymers bearing furan nuclei [5]. These polyols also have applications in fine chemistry. Having a certain number of properties useful in organic synthesis, such as chirality, rigidity, lipophilicity and hydrophilicity. These compounds may be used in the synthesis of a wide variety of molecules with potential biological activity [7,8].

II. MATERIALS AND METHODS

The main objective in this study is the valorization of hemicellulose contained in the nuclei of dates caused by industrial transformations of dates in other food products. Analysis of the various constituents of nuclei date showed their richness in glucomannans, hemicelluloses whose main chain is constituted by mannose,substituted with glucose and xylose[9].

The first part focuses on the extraction of hemicellulose from the nuclei. Then their hydrolysis. The second part is devoted to the transformation of monosaccharides obtained in furan polyols. The synthetic strategy is based on the condensation of the sugar with ethyl acetoacetate in an alcoholic medium with the presence of CaCl 2 as catalyst (Fig2).

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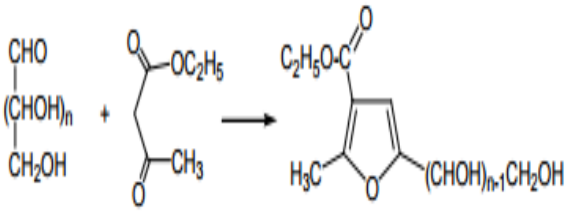
H. El Mahdi, Bioorganic Chemistry and Macromolecular Laboratory, Faculty of Science and Techniques, Université Cadi Ayyad, Marrakech, Morocco

Z. Abkhar, Bioorganic Chemistry and Macromolecular Laboratory, Faculty of Science and Techniques, Université Cadi Ayyad, Marrakech, Morocco

M.Taourirte, Bioorganic Chemistry and Macromolecular Laboratory, Faculty of Science and Techniques, Université Cadi Ayyad, Marrakech, Morocco

Y.Bachara, Bioorganic Chemistry and Macromolecular Laboratory, Faculty of Science and Techniques, Université Cadi Ayyad, Marrakech, Morocco



Glucose and Mannose (n=4) Ethyl acetoacetate Polyol furan

Fig 2: Synthesis of furan polyols from Glucose and mannose

III. EXPERIMENTAL PART

I- PRETREATMENT NUCLEI OF DATES Treated nuclei of dates come from a southern Saharan region (Zagoura) The sample washed, dried and then frozen at a temperature below 4 ° C to facilitate its grinding. The sample undergoes dilipidation, extraction with ethanol then hot water to remove extractable consisting mainly by tannins, free sugars and proteins.

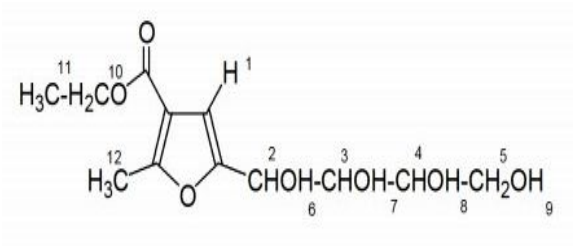
1 -Dilipidation 100g mechanically crushed nuclei are introduced into a stirred reactor and thermostatically containing 500ml of hexane. The whole is heated at 40 ° C for 120 min. The solvent containing oil is withdrawn from the reactor and evaporated by a rotary evaporator to isolate oil. 2- Extraction with ethanol This step allows the removal of free sugars (glucose, fructose, sucrose) and a large part of the tannins. The Dilipided sample is heated to 60 ° C with stirring for 3 hours in 500 ml of ethanol. Then cooled and filtered. The residue obtained

is dried in an oven at 40 ° C for 5 hours. 3- Extraction with hot water The ethanol extracted residue is heated for 2 hours at 100 ° C in 500ml of distilled water. This extraction step is redone a second time under the same conditions, in order to remove most of the pectins. The residue obtained is dried in an oven at 40 ° C. II- EXTRACTION OF HEMICELLULOSE The residue is refluxed for 3 hours in 200 ml of an acetic acid / formic acid / water mixture, in the proportions of 120, 40, 40 (by volume). After filtration of the reaction mixture, the filtrate is evaporated under vacuum until elimination of 50% of its volume. After adding ethanol to the solution, hemicelluloses precipitate spontaneously. They are separated by filtration. III- HYDROLYSIS OF HEMICELLULOSES. Hemicelluloses obtained undergo hydrolysis with hydrochloric acid solution (2.5%) for 45 min in 110 ° C. By filtration, we recovered the sugar juice. The remaining solid residue is mainly cellulose. The juice obtained contains 25% mannose and 12% of glucose relative to the solids initially introduced IV- SYNTHESIS OF FURAN POLYOLS. No special treatment is applied to the hydrolyzate. Only neutralization then evaporation to bring it to the desired rate of hydration. The syrup obtained is introduced in the presence of an organic solvent (ethanol 80% + water 20%) in a reactor fitted with a condenser and a mechanical stirrer. Then calcium chloride is added (CaCl2 / sugar = 3) and finally the acetyl ethyl acetate (β-keto ester / sugar = 1.25). The mixture is heated at 75 ° C for 5 hours.

IV. RESULTS AND DISCUSSION

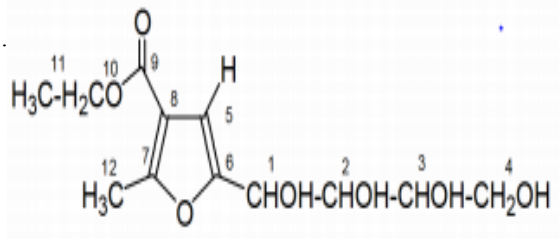
The yield of furan polyol is of 90% compared to the sugars in the hydrolyzate. Finally the reaction mixture is dissolved in water, the furane polyol derived from glucose and mannose precipitated, then isolated by filtration. The dosage of the constituents of the mixture obtained after reaction is carried out by high performance liquid chromatography (HPLC)

Measurements of optical rotations are performed on a Perkin Elmer with methanol as solvent. The 1H and 13C NMR spectra were performed on a Brucker 300 WM type apparatus in DMSO as solvent. Structural identifications furan polyols. Polyol furan from mannose and glucose: Optical rotation function: (α) 25 589 = -14.8 ° C 1 H NMR (DMSO-d6, 300 MHz Bruker) (δ ppm):



6.45 (s, 1, CH), 5.12 (d, J = 9 Hz, 1, H1), 4.34-4.73 (m, 4H, H2, H3 et H4), 4.16 (q, J = 9Hz, 2H, CH2), 3.39-3.61 (m, 4H, H5, H6, H7, H8), 2.5 (s, 3H, CH3), 1.3 (t, 3H, CH3).

RMN 13C (DMSO-d6, Bruker 300 MHz) (δ ppm) :



13.99 (C11),14.78 (C12), 60.23 (C10), 63.88 (C4), 66.43 (C3), 71.52 (C2), 73.06 (C1), 107.16 (C5), 113.89 (C7), 156.01 (C6), 157.54 (C8), 163.88 (C9)

CONCLUSION

The valorization process of the plant material we adopt in this work is very advantageous since it allows obtaining different products at each step of refining, with various applications in chemical industry, food processing and fine chemicals such as: -Proteins and lipids that are used in the food industry, pharmacy or cosmetology and in the field of macromolecules. -Celluloses: which can be a raw material for the manufacture of materials and chemical cellulose. -Furan polyols: products for fine chemicals and monomers for polymerization.

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