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Cyclooligosaccharide modification applying microwaves. The case of β -cyclodextrin esterification

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ABSTRACT

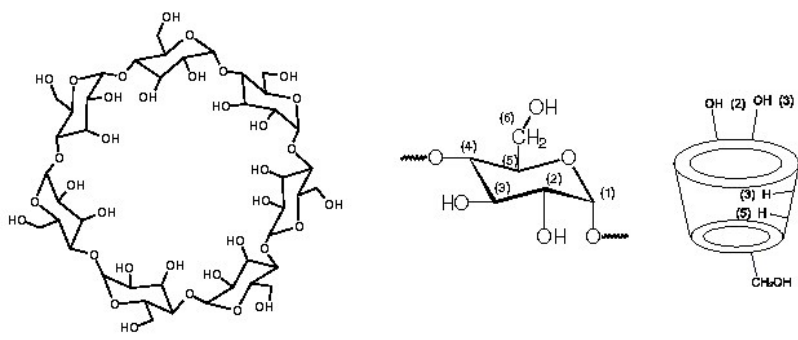
Some preliminary studies on microwave-assisted chemical modification of cyclodextrins are presented. As a chemical linkage agent a citric acid was applied. The esterification reaction of cyclodextrin with polycarboxylic acid was controlled by means of HPLC as well as a spectroscopic method for product complexation ability.

KEYWORDS

cyclodextrin, citric acid, esterification, microwaves

INTRODUCTION

Cyclodextrins are the cyclic oligosaccharides built by several anhydroglucose units (AGU), that are jointed together and form a kind of cone. The most commonly used CD's consist 6 to 8 AGU respectively [1]. Described molecular structure involves the ability of CDs to form some inclusion complexes with many organic and inorganic moieties. The cone-like architecture of CD results in the phenomenon of hydrophobic character of the inner space of this carbohydrate. Formation of the complex causes the increase in water solubility as well as decrease in volatility and sublimation tendency of small molecules. Nowadays, CD's complexes find a lot of applications in both practical and laboratory aspects. According to molecular encapsulation mechanism they are applied in the field of stabilisation of vitamins and flavour compounds in food and serve as an important matrix in production of drugs with long realising time. They also find the important place in analytical chemistry, organic synthesis, cosmetics and agriculture. CD's grafted on polymers backbones may also serve as a potential matrix in textil industry and allow to realase some medicines, flavours or absorb sweat etc [2].

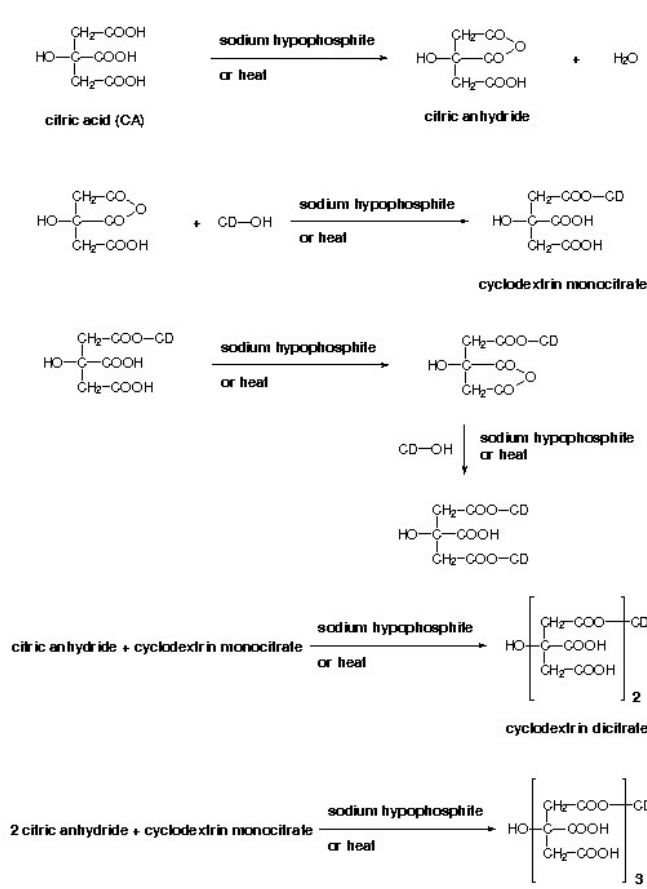


Scheme 1: Molecular structure of β -cyclodextrin.

From the other hand, microwave synthesis is a new technique for conducting chemical reactions. Acceleration of organic reactions by microwaves has been proven, and in many cases, microwave techniques have become more effective than conventional processing. The phenomenon originates in: interaction of electromagnetic field with the matter by means of dielectric and/or conducting mechanism [3]. As a continuation of our previous works on microwave assisted organic transformation [4], including some esterification processes [5], we would like to present some preliminary studies on CD esterification with polycarboxylic acid i.e. citric acid (CA). Product of β -CD modification is going to have ester-like structure and may serve for modification of biopolymers possessing free hydroxyl groups, capable to be esterified including e.g. starch, cellulose etc. Such kind of modifications, that are very often the main part of textile and food products processing, gives the opportunity to create the new class of "poly-nanomaterials" with specific functional properties.

EXPERIMENTAL

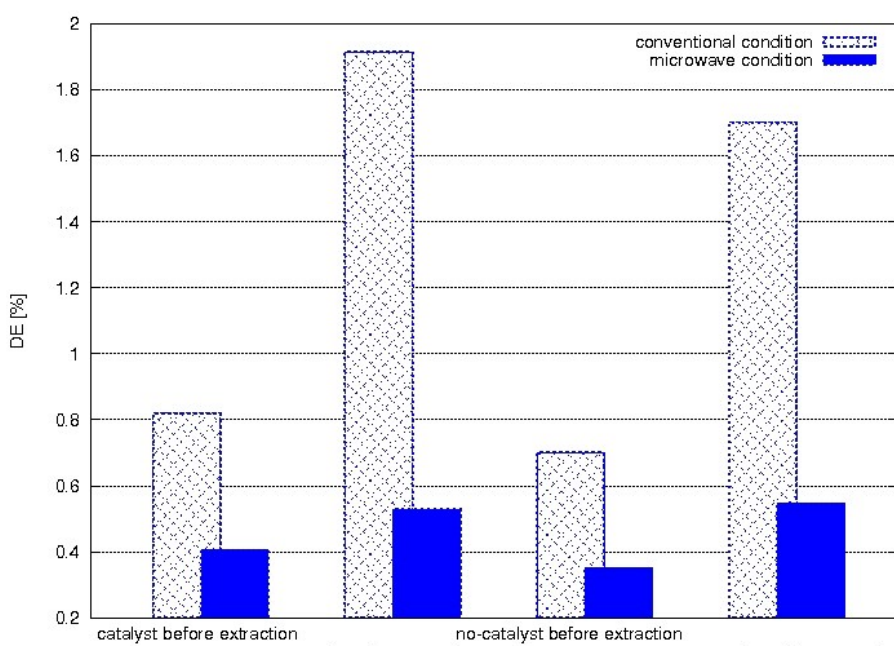
All the reactions were performed according to Scheme 2 proposed by [6]. CA (9mmol), β -cyclodextrin (9mmol) and catalyst (sodium hypophosphite - 6mmol) were dissolved in water (4mL). The paste was put on a plate and heated at 130°C for 2 hours. After the reaction was finished all the products (BCD-CTR) were weighted and purified by extraction with 2-propanol (12hours). Subsequently all the reactions were carried out employing microwave irradiation. The set-up of the microwave assisted process was similar to conventional ones. The reaction paste was irradiated in Moulinex 850W typ MICRO CHEF FM A945821 GS microwave reactor at 90W. The reaction time was 10min. Temperature of the reaction was monitored by means of fiberoptic temperature detector RFX-2 Reflex (Fiso, Canada) and reaches about 160°C for catalytic process and 115°C when no catalyst was added. Reaction mixture was purified as was described for conventional processes. All the reaction products were analysed by means of HPLC (column: Lichrospher NH2; Knauer, detection RI; Knauer, eluent: a mixture of 0.001mol/L H2SO4 with 1% NaNO3, flow 1mL/min) as well as complexation ability (spectrophotometric analysis of phenolphthalein-cyclodextrin complexes in alkaline solution). The reducing power as a significant factor of CD's thermal and hydrolytic stability were performed by means of DNS method [7]. Additionally, the analysis of quantity of hypophosphite ions in final products, were done.



Scheme 2: β -cyclodextrin esterification route [6].

RESULTS AND DISCUSSION

As a result of our investigation a series of new materials were obtained. Chromatographic analysis clearly shows that, however there is significant yield of reaction (Table 1), the selectivity of the process is higher in microwave assisted conditions. The yield of microwave enhanced reactions reaches about 10% (by means of peaks area) when in conventional processes there was no reaction products detected in the system. Obtained results of conventional reaction seems to be rather curious by means of results presented by El-Tahawy at all [6]. Such kind of results forced us to optimise the microwave process that up to now seems to be very promising. The full confirmation of the product structure will be done soon.



Scheme 3: Dextrose Equivalent (DE) of selected ester as a measure of oligosaccharide ring decomposition.

In all other investigated cases the selectivity is very poor. In order to discover the mechanism of any changes in carbohydrate ring constitution the analysis of reducing power was performed. When the cyclodextrin ring is going to open a significant increase in reducing power (by means of DE factor) should be observed due to free aldehyde group at the end of the carbohydrate chain. Result of investigation showed that Scheme 3 proved, that some part of cyclic carbohydrates is going to be destroyed. It was observed that such kind of destruction was established for all conventionally heated samples. Contrary, the microwave assisted process, does not influence on reducing power at all.

Table 1: Results of microwave assisted esterification of cyclodextrin by citric acid.

ID	Yield [%]	Ability to form an inclusion complex [%] ¹	Amount of catalyst found in the sample [mg] ²
Δ - no catalyst	85.9	84.1	0.003/0.000
Δ - with catalyst	95.7	76.1	4.300/5.170
MW - no catalyst	87.2	80.0	0.004/0.000
MW - with catalyst	94.1	77.3	3.870/5.080
MW - no catalyst ³	.4	88.1	6.760/6.820
MW - with catalyst ³	.4	79.6	0.007/0.000

¹ - Ability to form an inclusion complex compared to those obtained for β -cyclodextrin

² - Amount of catalyst found in the sample compared to theoretical value

³ - Parametres estimated after extraction in 2-propanol

⁴ - Not determined

One of the most important factor, when focusing on cyclodextrin modification and application, seems to be the complexation ability. Synthesis of cyclodextrin derivatives, that is investigated by any side group, is interesting from the scientific point of view but is presently useless when trying to find any application. The results of our investigation shows that reaction products are still able to form some inclusion complexes. Complexation ability is slightly lower but still at acceptable level. Observed decrease has its origin in citric acid molecule that is linked with CD ring, what, due to its shape and dimensions, may sometimes block the inner space of cyclodextrin.

After purification of the product, BCD-CTR was analysed according to its structure, and complex ability. The results forced us to conclude that BCD-CTR may be very helpful as polysaccharide modification precursors that still possess some complexation ability. Further studies on BCD-CTR will also cover the optimisation of synthetic procedure, including some kinetic investigation as well as grafting of obtained esters on polysaccharides chains.

LITERATURE

- [1] J. Szejtli; Introduction and General Overview of Cyclodextrin Chemistry; *Chemical Review*; **1998**; 98, 5, 1743.
 [2] a) Sz. Bednarz, W. Mazela, M. Pajda, M. Lukaszewicz; *Przegląd Włoknienny*; **2008**, 62 2, 58. b) A. R. Hedges; *Chemical Review*; **1998**; 98, 5, 2035.
 [3] For relevant papers and reviews on microwave assisted chemical reactions see: a) D. Dallinger, O. Kappe, *Chemical Reviews*, **2007**, 107, 6, 2563. b) O. Kappe, M. Matloobi, *Combinatorial Chemistry and High Throughput Screening*, **2007**, 10, 9, 735. c) A. Loupy, *Microwaves in Organic Synthesis*, **2006**, Wiley-VCH. d) D. Bogdal, A. Loupy, *Organic Process Research and Development*, **2008**, 12, 4, 710. e) D. Bogdal, *Microwave-assisted Organic Synthesis, Volume 25: One Hundred Reaction Procedures*, **2006**, Elsevier Science. e) A. K. Bose, M. S. Manhas, S. N. Ganguly, A. H. Sharma, B. K. Banik; *Synthesis*; **2002**, 1578, 159.f) L. Perreux, A. Loupy; *Tetrahedron*; **2001**, 57, 9199.
 [4] a) M. Lukaszewicz, Sz. Bednarz, A. Ptaszek, I. Gerlich, A. Bednarz, D. Bogdal, B. Achremowicz.; *11th International Electronic Conference on Synthetic Organic Chemistry*, Basel, Switzerland **2007**. b) D. Bogdal, S. Bednarz, M. Lukaszewicz, *Tetrahedron*, **2006**, 62, 9440. c) Marcin Lukaszewicz, Bohdan Achremowicz, Szczepan Bednarz, *9th International Electronic Conference on Synthetic Organic Chemistry*, Basel, Switzerland **2004**. d) Sz. Bednarz, M. Lukaszewicz, B. Achremowicz, M. Grzesik, D. Bogdal, *The 5th International Congress of Food Technology*, **2007**, Thessaloniki, Greece. e) D. Bogdal, M. Lukaszewicz; *Synlett*, **2000**, 1, 143.
 [5] D. Bogdal, I. St&Amp;pieÄ, M. Pajda; *Polish Journal of Chemical Technology*; **2003**, 5, 3, 90.
 [6] Khaled El-Tahawy, Mohamed A. Gaffar, Safaa El-Rafie; *Carbohydrate Polymers*, **2006**, 63, 385.
 [7] G.L. Miller; *Anal. Chem.* **1959**, 31, 3, 426.

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