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MODERN ENGINEERING TECHNIQUES FOR THE PRODUCTION OF MODIFIED POLYSACHARIDES WITH BIOLOGICAL ACTIVITY

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ABSTRACT

Esters are used in the industry. The rapid increase in demand for esters in the food, cosmetics and pharmaceutical industries makes it mandatory to find alternative ways of synthesis instead of low-yield, expensive, energy-intensive and prolonged reactions.

The production process for the synthesis of esters is based on chemical esterification of fatty acids with alcohol in the presence of inorganic catalysts at high temperatures. However, these chemical processes are non-selective and consume a large amount of energy. In this regard, the current situation of environmental degradation requires the development of efficient and environmentally friendly methods in terms of energy consumption and waste reduction. The synthesis of esters by sonication is also an economical and effective method of performing esterification with broad practical application.

The article presents a review of research and modern engineering solutions based on "green technologies" for the synthesis of esters. Significant advantages of the method of transesterification of methyl caprate with sucrose, leading to esters with potential biological activity such as antifungal and antimicrobial agents, are highlighted.

Key words: polysaccharides, esterification, ester, ultrasonic, sonochemistry, capric acid.

INTRODUCTION

Sonochemistry is a modern strand of green chemistry, using ultrasonic energy to conduct chemical processes. The key advantages of sonochemistry are increasing reaction selectivity, reducing reaction time, using less hazardous chemicals and solvents, reducing energy consumption, conducting processes under softer conditions, etc. These advantages increasingly require the use of ultrasonic impact to manage chemical reactions stimulating higher efficiency and effectiveness. Sonochemistry is unique due to the phenomenon of cavitation – through the formation, growth and implosion of gas bubbles in the liquid. During the decay of microbubbles as a result of cavitation, high pressure and temperature are generated inside them. This energy provides an opportunity for interaction of substances (Mason, T., D. Peters 2011, Zhong et. al. 2009, Nguyen et. al. 2021, Song et. Al. 2006).

Esters are widely used in the industry – food additives, plasticizers in plastics, precursors in medicinal products, etc. The rapid increase in demand for esters in the food, cosmetics and pharmaceutical industries makes it mandatory to find alternative ways of synthesis instead of low yield reactions, expensive, energy-intensive and prolonged (Baker et. Al. 2000, Galdeano et. Al. 2009, Galdeano et. Al. 2009, Veiga-Santos et. Al. 2007)

One of the classic methods of modifying polysaccharide molecules is esterification, which consists in the interaction of carboxylic acid and alcohol in the presence of acid as a catalyst that can be sulphuric, *p*-toluenesulfonic acid etc. This type of process is slow, non-selective, consumes a large amount of energy and has low performance (Lara-Cerón et. Al. 2020, Zhang et. Al. 2020, Deng et. Al. 2006, Dan et. Al. 2009, Yongshi et. Al. 2013).

Most higher fatty acids have fungicidal action and are used as antimicrobial agents, initially in the production of soaps. Over the past 50 years, however, they have found both in vitro and inhibitors in food products and as topical and systemic antifungal agents (Zhong et. Al. 2009, Yuyun et. Al. 2009).

Unsaturated undecylenic esters of sucrose show very good antimicrobial activity relative to Candida albicans, exhibit inhibitory activity against Gram-positive bacteria: Bacillus subtilis and Bacillus cereus, and Gram-negative E. coli inhibiting the growth of Pseudomonas aeruginose, against which undecylenic acid was inactive. Based on this study, sucrose undecylenic and sucrose laurate ester can be used as a potentially antimicrobial remedy for plants and foods against certain microorganisms.

As far as it is known, inulin acetate is less studied for antimicrobial activity compared to sucrose esters. Inulin acetates with DA 2.5 and 3.0 1 mg/ml showed moderate antimicrobial activity against food-born pathogens Listeria monocytogenes ATCC 8632 and Staphylococus aureus 745 at low concentration. Its activity is comparable to the control antibiotic Bisepthol. Saturated palmitic esters of sucrose and fructooligosaccharides do not exhibit antimicrobial activity. Unsaturated esters of sucrose and fructooligosaccharides can be applied as potential antimicrobials, not only in food preservation, but also in medicine and cosmetics for the preparation of antifungal ointments for the treatment of diseases caused by *Mycobacterium smegmatis* and *Candida albicans* (Vargas et. Al. 2020, Petkova et. Al. 2017).

The purpose of this article is to apply ultrasonic energy in transesterification to obtain potentially biologically active polysaccharide esters – capric acid sucrose esters.

EXPERIMENTAL

Methylcaprate synthesis

Place 30.3 g of capric acid in a round-bottomed flask with a ground. Add 250 cm^3 hexane and 1 $dm^3$1% H_2SO_4in CH_3OH. Connect the flask to a water-cooled reflux condenser and heat in a water bath at 68–70°C. After 120 minutes, the reaction is quenched and the reaction mixture is intensively cooled by adding 100 cm^3 of ice-cold distilled water and neutralisation is carried out with 10% Na_2CO_3. Perform a three-fold extraction of 50 cm^3 hexane. The collected extracts are dried with anhydrous Na_2SO_4. After filtration and distillation of the solvent under vacuum, separate the ester.

Conventional synthesis of sucrose caprate.

Place 50 cm^3 methanol and 0.018 mol of capric acid, sucrose and catalyst CH_3ONa (0,1 mol) in a 100 cm flask. The reaction flask was placed in a water bath at 40 and 65°C. The reaction temperature is controlled using a contact thermometer. The course of the reaction is tracked by TLC.

After completion of the reaction, distil the solvent under vacuum. Dissolve the residue in 25% NaCl / *n*-butanol (1:1) and divide the mixture with a separating funnel. Perform a three-fold extraction with 20 cm^3 *n*-butanol. The collected extracts are dried with anhydrous Na_2SO_4 and the solvent is distilled under vacuum.

Ultrasonic synthesis of sucrose caprate.

Place 50 cm^3 methanol and 0.018 mol of capric acid, sucrose and catalyst CH_3ONa (0.1 mol) in a 100 cm^3 flask. The mixture is sonicated at room temperature. The course of the reaction is tracked by TLC. After completion of the reaction, distil the solvent under vacuum. The residue was dissolved in 25% NaCl/*n*-butanol 1:1 and the mixture was separated by a separatory funnel. Perform a three-fold extraction with 20 cm^3 *n*-butanol. The collected extracts are dried with anhydrous Na_2SO_4 and the solvent is distilled under vacuum.

METHODS OF IDENTIFICATION AND CHARACTERIZATION

Infrared spectroscopy

IT spectroscopy with Fourier transformation was used to identify and characterize the resulting esters. The spectra were recorded on a *Nicolet Avatar* spectrometer (Termo Scientific, USA) in a KBr tablet, in the range of 4000–500 cm^{-1}.

NMR imaging

NMR spectra of (^1H and ^{13}C) of the synthesized esters were recorded on a Bruker spectrometer (500 MHz) in a solution of $CDCl_3$ and standard tetramethylsilane.

RESULTS AND DISCUSSION

Sucrose esters are synthesized by transesterification with a methyl ester of capric acid under conventional conditions and by ultrasonic impact.

In the spectra of the studied esters, several areas characteristic of carbohydrates stand out.

In the first of them, about 3300 cm^{-1} has a wide asymmetric band due to the valence vibrations of – OH. The strong interaction between the structural elements of the macromolecules in the modified sucrose is the reason in the spectrum considered, bands arise due to complex vibrations, which can be defined as oscillations of both the furanose ring and the macromolecule as a whole. Valent fluctuations (C – C). (C – O), (C – O – C) of the furanose structure are observed between 1000 and 1200 cm^{-1}.

Depending on the degree of substitution, the maximum of this strip is shifted and at the same time the half-width changes. This is due to the hydroxyl groups which form the hydrogen bonds as well as to the esterification of some of them.

In the infrared spectrum, a new stripe in the spectrum of esters at 1734 cm^{-1} due to valence oscillations ($\nu C{=}O$) of the ester is clearly evident. The presence of a similar strip at 1720–1728 cm^{-1} was reported by *Song* in sucrose octanoates (ester obtained by transesterification of sucrose with ethylcaprate) as well as in the spectrum of sucrose octanoate resulting from ultrasonic synthesis.

In ^1H MRI spectrum, two areas can be separated – in the range 0–2.36 ppm characteristic of methyl and methylene protons of acid and 3.39–5.40 ppm characteristic of the carb-cell proton shown in Table 1.

Chemical offset for methyl group protons in sucrose caprate is observed at 0.87~0.99 ppm.

Table 1: Chemical offset (δ, ppm) in ^1H NMR spectrum

Group	Chemical shifts, (δ, ppm)
$\mathbf{CH_3}$–	0.96~0.99
–$(\mathbf{CH_2})_n$–	1.31~1.68
–$(CH_2)_n$–$\mathbf{CH_2}$–O	2.34~2.36
-O-C**H**-O	5.39~5.40
H-Glc	3.39~5.40
H-Fru	3.62~4.52

Signals for methylene group protons are in the range of 1.17~2.02 ppm. Glucose protons of glucopyranos are observed in the range of 3.39~5.40 ppm and glucose protons of fructofuranosis at 3.62~4.52 ppm.

In ^{13}WITH MRI spectra, characteristic signals for a carbonyl carbon atom are observed at 174.36–175.12 ppm.

Table 2: Chemical offset (δ, ppm) in ^{13}C NMR spectrum

Group	Chemical shifts (δ, ppm)
H_3**C**–	14.02
–(**C**H_2)$_n$–	22.94~34.03
–**C**=O	174.36
C-Glc	62.26~94.71
C-Fru	61.18~108.18

The signals of the carbon atoms of the pyranose, respectively, of the furanose ring, are observed in the range 61.18–108.18 ppm, with carbon atoms from the pyranose ring being at the lower frequencies and for the furanose at the higher frequency range.

Ultrasonic impact leads to an increase in the yield of sucrose caprate by up to 12%. The presented results generally show that when the synthesis is carried out by ultrasonic treatment, the yield of the obtained sucrose esters is higher.

In order to optimize the conditions of the reaction of transesterification on the yield, the influence of the main parameters influencing the reaction time and the production of molar ratio ester: sucrose – 1:1 and 3:1 has been studied; catalyst type – CH_3ONa, K_2CO_3, NaH_2PO_4; mol catalyst ratio – 0,1; 0,3; 0,5.

Based on the comparative analysis of the catalyst data used in conventional and ultrasonic synthesis, it can be concluded that the more suitable catalyst is CH_3ONa. The use of sodium dihydrogen phosphate does not lead to a significant increase in the yield of sucrose caprate.

Under the chosen reaction conditions, the change in the catalyst molar ratio results in a slight increase in the yield. For this reason, experiments were conducted primarily when using a molar ratio of catalyst to sucrose 1:1. A threefold increase in the amount of ester results in a slight increase in yield, which indicates that the amount of sucrose limits the reaction time.

Unsaturated 10-undecilene esters of sucrose and fructooligosaccharides demonstrate significant antimicrobial activity relative to *Candida albicans*. These sucrose esters are more active than 10-undecilenic acid, well known for its strong antibacterial and antifungal activity. For the first time, the antimicrobial activity of the esters of fructooligosaccharides has been established. It is clearly shown that the 10-ounce ester of sucrose and fructooligosaccharides inhibits the growth of gram-positive bacteria *Bacillus subtilis* and *Bacillus cereus* and Gram-negative *E.coli.* Only sucro-10-undecilene ester inhibits the growth of *Pseudomonas aerugenose*, against which 10-undecilene acid is inactive (Vassilev et. Al. 2016, 2018, 2020, 2021, Petkova et. Al. 2017).

Due to proven antibacterial and antifungal activity, inulin acetates can be successfully applied in cosmetics, medicine and agriculture due to their better antifungal activity against *Aspergillus niger, Fusarium oxysporum and Penicillium sp.*

Similarly to undecylene, inulin and fructooligosaccharide esters (Vassilev et. Al. 2016, 2018, 2020, 2021, Petkova et. Al. 2017), it is expected that sucrose caprates synthesized according to the method described in the article should also possess an antimicrobial and antifungal agent and may be used to develop a new plant protection formula and ecological fungicide. The promising ability to foam and emulsify offers an adequate solution to treatment and adhesion problems on root or leaf surfaces. These functional properties in combination with antimicrobial activity can also be successfully used for the administration of sucrose caprates in pharmaceutical preparations and for food preservation.

CONCLUSION

The intensifying effect of ultrasonic effect in the transesterification of methylcaprate with sucrose catalyst sodium methylate at room temperature has been demonstrated, in which sucrose caprate is obtained with a significant minimization of reaction time.

As a result, the reaction time is reduced and the reaction temperature is reduced. Under the conditions of ultrasonic synthesis, the composition of the resulting esters is the same as those obtained by the conventional method.

Unambiguously, with the help of chromatographic and spectral methods, it was found that under the selected fusion conditions there was no rupture of carbon-carbon bonds and auto-oxidation of the reaction product.

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