

PREPARATION OF NON-POLAR DERIVATIVES OF 1-MONOACYLGLYCEROLS

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ABSTRACT

Glycerol monoesters of oleic acid and lauric acid were synthesized. Their acetonides were prepared by the azeotropic distillation in benzene and p-toluensulfon acid was used as a catalyst. After the purification by crystallization in methanol products were tested by thin layer chromatography in system of chloroform: acetone: methanol. The proof of isopropyliden group in product was analyzed by IR spectroscopy. High instability of acetonides in storage time was proven. Also the stability of these acetonides was tested against hydrolysis.

Keywords: Monoacylglycerol, Acetonides, Purification

1. INTRODUCTION

Monoacylglycerols (MAGs) are widely employed in the food industry as emulsifiers [1]. Because of their antimicrobial properties they are also used in medicine and pharmacy, e. g. for controlled release of medicinal substances [2] Moreover, they are applied in other areas such as cosmetics and plastic industry [3]. Therefore, there has been increasing interest in the field of study of MAGs of fatty acids regarding both preparation and their potential applications. The one of the new perspective way how to prepare these derivatives is the addition of fatty acids with glycidol catalyzed with Cr(III)-complexes that causes nucleophilic opening of glycidol ring [4]. Despite the high benefits of this reaction, which include a high conversion, it is necessary to clean up residues from toxic glycidol and catalyst. One of the possibilities for subsequent purification from undesirable non-polar products is the decreasing of polarity. Transferring of liquid monoacylglycerols to solid products, which easily crystallizing, could be performed by the suitable derivatization. Therefore, the preparation of acetonides of monoacylglycerols (primary esters of lauric and oleic acids) is the main object of our research. This work deals with the preparation of monolauroylglycerol (MAG C_{12:0}) and monooleylglycerol (MAG C_{18:1}) and their acetonides.

2. MATERIALS

Glycidol, carboxylic acids (oleic and lauric), chloroform, toluene, methanol, chromium(III) acetate hydroxide (CH₃COO)₃Cr₃(OH)₂, were purchased from Sigma-Aldrich and were used without further purification. Other chemicals (acetone, ethanol, p-toluensulfon acid and glycerol) were of analytical purity.

3. METHODS

Monoacylglycerol was prepared by the reaction of fatty acid with glycidol in the presence of Cr(III) complexes as catalysts. The reaction was carried out in a glass reactor provided with a magnetic stirrer reflux condenser and a temperatur-stabilized jacket enabling to control the reaction temperature. Catalyst a subsequently glycidol were added to the melt of corresponding fatty acid in required quantity at a given temperature. Glycidol was introduced at 12% mole excess to the fatty acid. The used amount of catalyst was 0,5% of the glycidol-fatty acid reaction mixture weight [4].

Acetonides of monolauroylglycerol and monooleylglycerol were prepared by azeotropic distillation in benzene, by p-toluensulfon acid catalysis [5]. Reactive mixture consisted of waterless acetone and recrystallized corresponding monoacylglycerol in a molar rate 1:1,1. The quality of products was tested by thin layer chromatography (TLC) so, thus approximately 6 μ l of given substance was applied to silica gel plates. After the solvent evaporation from the applied sample, plates were developed vertically in a appropriate solvent system, in a developing chamber, which was covered by the lid, so that no evaporation occurred. After taking from the chamber, the plates were dried and evenly sprayed with detection agent (0,2% 2,7-dichlorfluorosein). Spots of individual substances were indicated under UV lamp at 366 nm.

Acetonide of monolauroylglycerol was also analysed by IR spectroscopy. The stability of this acetonide was also tested against hydrolysis.

4. RESULTS

The monoacylglycerols were produced in conversion 97,2% (monolauroylglycerol) and 87,3% (monooleylglycerol). The next step was the preparation of corresponding acetonides by azeotropic distillation in benzene. These products were further tested by thin layer chromatography (TLC). As can be seen in Figure 1, in case of monolauroylglycerol acetonide five splodges occurred. The first one belonged its monoacylglycerol and the second one its acid. The others haven't been identified yet.

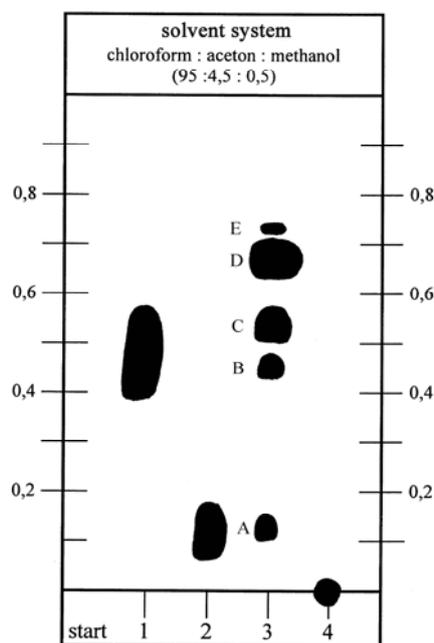


Figure 1. Chromatogram: 1=lauric acid, 2=monolauroylglycerol, 3= monolauroylglycerol acetonide (A=lauroylglycerol, B=lauric acid, C, D, E=still unidentified), 4=glycerol

For the identification of others splodges more experiments had to be done. They included also blank test (Figure 2.). As you can see in this chromatogram, the splodge D is missing. From this fact, it is clear, that the splodge D belongs to acetonide.

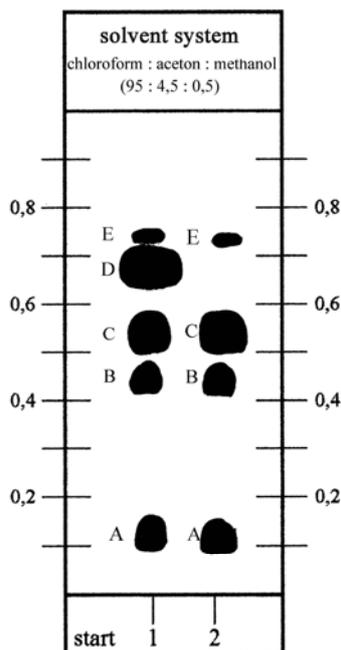


Figure 2. Chromatogram: 1=monolauroylglycerol acetonide (A=monolauroylglycerol, B=lauric acid, C=dilauroylglycerol, D=acetonide, E=trilauroylglycerol), 2=blank test (A=monolauroylglycerol, B=lauric acid, C=dilauroylglycerol, E=trilauroylglycerol)

In contrast to monolauroylglycerol acetonide, seven splodges occurred in the case of monooleylglycerol acetonide (Figure 3.). The splodge F belongs to acetonide.

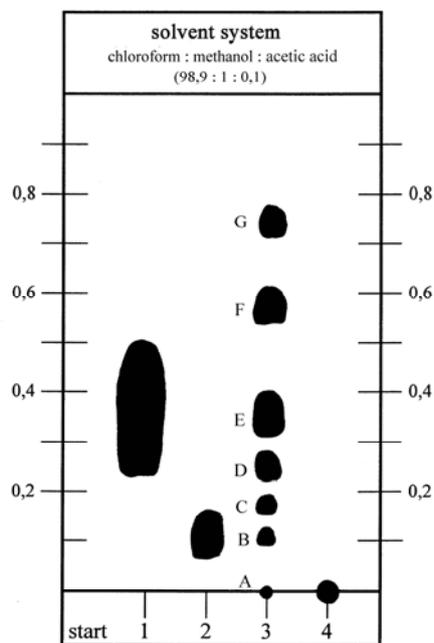


Figure 3. Chromatogram: 1=oleic acid, 2= monooleylglycerol, 3= monooleylglycerol acetonide (A=glycerol, B=monooleylglycerol, C=2-monooleylglycerol, D=1,2, resp. 1,3-dioleylglycerol, E=oleic acid, F=monooleylglycerol acetonide, G=trioleylglycerol), 4=glycerol

Further, IR spectroscopy was done only for monolauroylglycerol acetonide due to its solid consistence contrary to monooleylglycerol acetonide. Unfortunately, the presence of acetonide group wasn't proved in consequence of hydrolysis in measuring time. In the last step, testing of stability

against hydrolysis (high-temperature and cold- temperature hydrolysis) was carried out. In both cases, results showed many side products.

5. CONCLUSIONS

In conclusion, monolauroylglycerol and monooleylglycerol acetonides were produced. However, their preparation was too complicated process because of the formation of appendant reactions, e.g. reverse hydrolysis, reesterification, intramolecular reverse fault etc. Therefore it is necessary to focus on the further parameters for hydrolysis optimization.

6. ACKNOWLEDGEMENT

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