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Short communication

Monitoring the esterification of sorbitol and fatty acids by gas chromatography

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Abstract

Lauric acid esters of sorbitol, 1,4-sorbitan and 1,4:3,6-isosorbide were synthesized in laboratory. Esterification was carried out at 160°C with a catalyst for sorbitol cyclization and esterification, viz., *p*-toluenesulfonic acid. Lipid classes and polyols were separated and analysed by GC as trimethylsilyl ethers and esters. The purpose of the study was to determine the suitability of GC analysis of these products as a means of following the progress of reactions. The results confirmed the possibility of monitoring lauric acid and sorbitol esterification via the GC determination of lauric acid concentration.

1. Introduction

Non-ionic surfactants with ester groups (NSEG) such as sorbitan fatty acid esters (SFAE) are widely used as emulsifiers and stabilizers in the food and cosmetics industries. They are usually complex mixtures, because they have varying distributions of the alkyl chain length of the fatty acids.

Chemically, SFAE are complex mixtures of fatty acid esters of several polyols derived from sorbitol. These compounds are prepared by heating sorbitol and fatty acids at 160°C in the presence of a catalyst such as *p*-toluenesulfonic acid (*p*-TSA).

Two of the known polyols other than sorbitol itself are its anhydride, 1,4-sorbitan (1,4-anhydro-D-sorbitol), and the dianhydride, 1,4-3,6-isosorbide (1,4:3,6-dianhydro-D-sorbitol). The polyols are esterified, with and without cyclization at 160°C, with fatty acids, resulting in a complex mixture of mono-, di- and tri-fatty acids esters (Fig. 1).

SFAE have been determined by means of thin-layer chromatography (TLC) [1–4], gas chromatography (GC) [1,5–7] and high-performance liquid chromatography (HPLC) [8]. However, TLC has poor separation and quantitative capabilities and SFAE of high molecular mass cannot be measured by GC because they are non-volatile. Many studies have been reported on the application of HPLC to SFAE, as HPLC is very suitable for the determination of non-volatile compounds [8].

This paper describes a simple solution to the monitoring of synthetic and production activities.

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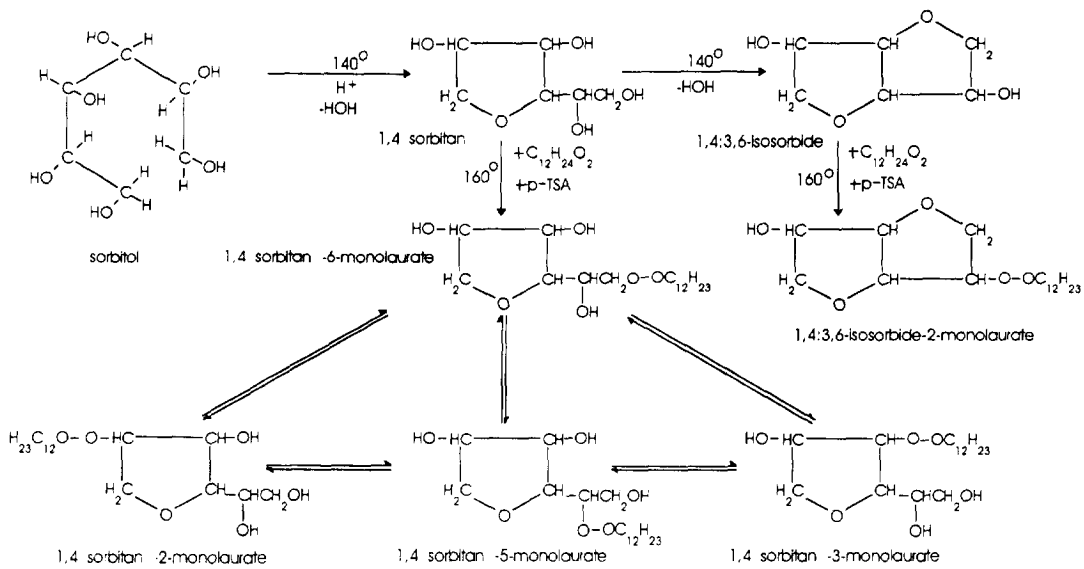

Fig. 1. Esterification of sorbitol with lauric acid with *p*-TSA as catalyst at 160°C.

Silyl derivatives are probably the most widely used derivatives for GC applications. Usually they are formed by the replacement of the active hydrogens of acids, alcohols, thiols, amines, amides and enolizable ketones and aldehydes with trimethylsilyl groups. The reaction of hydroxyl groups and carboxylic acids present in surface-active agents with hexamethyldisilazane and trimethylchlorosilane was used in this work [9]. The products are volatile trimethylsilyl ether and ester derivatives that are suitable for GC. The reaction is simple and quantitative without any undesirable side-reactions.

This paper describes the optimization of the GC separation. The extent of conversion of acid into sorbitan esters was calculated as mass-% (acid value) and vol.-% (GC analysis).

2. Experimental

2.1. Materials

The following were used: lauric acid ($C_{12}H_{24}O_2$), purum 98% (GC), (Fluka, Buchs, Switzerland), D-sorbitol ($C_6H_{14}O_6$), 99.5% (Hefti, Zurich, Switzerland), *p*-toluenesulfonic acid hydrate ($CH_3C_6H_4SO_3H \cdot xH_2O$) (Carlo Erba, Milan, Italy), Tri-Sil reagent (Pierce, Rockford, IL, USA), N,N-dimethylformamide, analytical-reagent grade (Merck, Darmstadt, Germany), Pyridine, analytical-reagent grade (Merck), 0.1 *M* KOH–ethanol (Kemika, Zagreb, Croatia), sorbitan monolaurate (Hefti) and 1,4:3,6-dianhydro-D-sorbitol (Aldrich, Milwaukee, WI, USA).

2.2. Apparatus

Analyses were performed using a Perkin-Elmer Model 8410 gas chromatograph with a flame ionization detector and fitted with a glass column [2 m × 5 mm I.D., packed with 3% SE-30 on Chromosorb G (60–80 mesh)] [7]. The column temperature was programmed from 150 to 220°C at 5°C/min. The injector and detector temperatures were 240°C. The carrier gas (nitrogen) flow-rate was 30 ml/min. The sample injection volume was 0.4 μl.

2.3. Preparations of esters

Individual fatty acid esters were prepared in the laboratory by two procedures. Sorbitol and

lauric acid (1:1, w/w), in the presence 0.1% w/w *p*-toluenesulfonic acid as catalyst were esterified at 160°C (method A, without cyclization) [10]. The reaction course was followed by taking samples after 15, 30, 45, 60, 90, 120 and 150 min determination of acid value and chromatographic analyses.

Sorbitol was cyclized with *p*-toluenesulfonic acid at 140°C (1 h) and esterified with lauric acid (1:1, w/w) at 160°C (method B, with cyclization) [11]. The reaction course was followed as in method A.

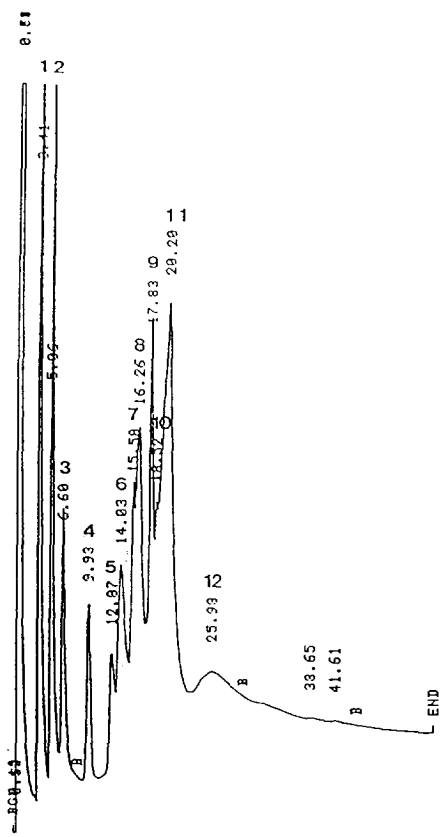

Fig. 2. Chromatogram of TMS derivative of cyclized sorbitol (method B) on a glass column (2 m × 5 mm I.D.) packed with 3% SE-30 on Chromosorb G (60–80 mesh). Column temperature, increased from 150 to 220°C at 5°C/min; carrier gas (nitrogen) flow-rate, 30 ml/min. Retention times (min) are shown on the peaks. Peaks: 1 = 1,4:3,6-isosorbide (1,4:3,6-dianhydro-D-sorbitol); 2 = 1,4-sorbitan (anhydro-D-sorbitol); 3–11 = unspecified isomers of cyclized sorbitol; 12 = unreacted sorbitol.

2.4. Preparation of derivatives

The samples withdrawn from reactor were silylated with Tri-Sil reagent. The reagent contains hexamethyldisilazane (HMDS) as the active ingredient, trimethylchlorosilane (TMCS) as catalyst and pyridine as solvent, all premixed in the appropriate proportions (2:1:9). The TMS derivatives were prepared by treating 50–60-mg samples [1] in N,N-dimethylformamide (DMF). Tri-Sil reagent (0.1 ml) and 0.3 ml of ester dissolved in DMF were added and shaken and allowed to stand for 15 min [1,5,7]. The supernatant (0.4 μl) was injected into the gas chromatograph. The amount injected was required for packed column application.

The assignment of peak 1 (Fig. 2) and peak 3 (Fig. 3) in the chromatograms was made according to chromatograms of standard compounds.

2.5. Conversion of fatty acids

The extent of conversion of acid into sorbitan esters was determined as follows: samples of the reaction mixture were taken periodically during the reaction, and the concentration of the residual fatty acid was determined GC and by titration with 0.1 *M* KOH–ethanol. The extent of conversion was calculated [4].

3. Results and discussion

The purpose of this study was to show possible ways of following the course of esterification reactions using GC. In this way it was possible to show which of the isomers present undergoes the esterification reaction with lauric acid. The conversion of lauric acid was determined, and the presence of cyclized sorbitol isomers was defined using GC.

Fig. 1 shows the hypothetical sequence of the esterification reaction up to monolaurate on the basis of the results obtained using GC. Fig. 2 shows gas chromatogram of the cyclized sorbitol with the corresponding isomers and their retention times (method B). The retention times of individual specific isomers, isosorbide and 1,4-

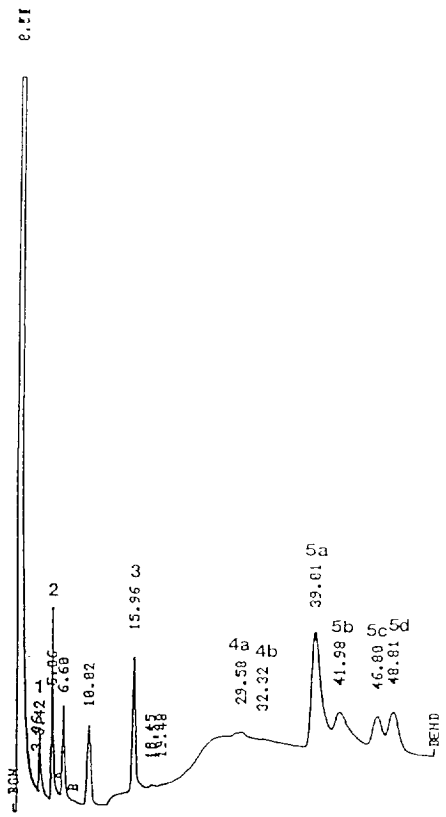

Fig. 3. Chromatogram of TMS derivative of reaction mixture of sorbitan monolaurate (method B) on a glass column (2 m × 5 mm I.D.) packed with 3% SE-30 on Chromosorb G (60–80 mesh). Conditions as in Fig. 2. Retention times (min) are shown on the peaks. Peaks: 1 = 1,4:3,6-isosorbide; 2 = 1,4-sorbitan; 3 = lauric acid, 4a and b = 1,4:3,6-isosorbide monolaurate; 5a–d = sorbitan monolaurate.

sorbitan, were separately determined [1,6] and compared with the mixture of isomers of cyclized sorbitol. The retention time of 1,4:3,6-isosorbide (peak 1) was 3.41 min and that of 1,4-sorbitan (peak 2) was 5.06 min. These compounds are present at higher concentrations in the mixture of cyclized sorbitol relation in comparison with other isomers.

The gas chromatogram of sorbitan monolaurate (prepared by method B) with characteristic peaks of sorbitol anhydrides (peaks 1 and 2), lauric acid (peak 3) and sorbitan monolaurate (peaks 4a and b and 5a–d) is shown in Fig. 3 [1,6]. Peaks 4a and b represent possible isomers

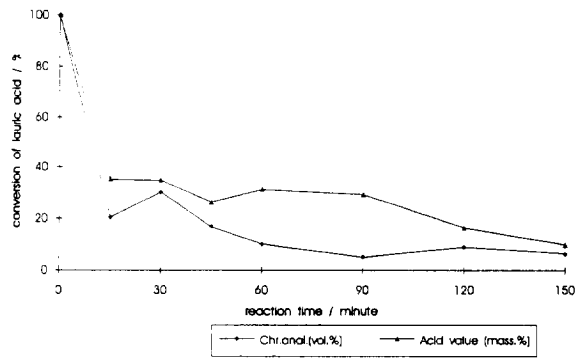

Fig. 4. Change in concentration of lauric acid reacted in the course of reaction with sorbitol at 160°C without previous cyclization of sorbitol with *p*-TSA as catalyst. ◆ = GC analysis (vol-%); ▲ = acid value (mass-%).

of sorbitan monolaurate obtained by the esterification reaction of 1,4:3,6-isosorbide with lauric acid. Peaks 5a–d could represent isomers of sorbitan monolaurate obtained by the esterification reaction of 1,4-sorbitan with lauric acid [1]. The retention time of lauric acid standard was separately determined (peak 3) [1,6]. The retention times of mono-, di, tri- and tetralaurates obtained by the esterification reaction of sorbitol anhydrides with lauric acid were theoretically explainable.

Figs. 4 and 5 show the conversion of lauric acid with [11] (method B) and without [9] (method A) previous sorbitol cyclization, as obtained using GC (vol.-%) and by determi-

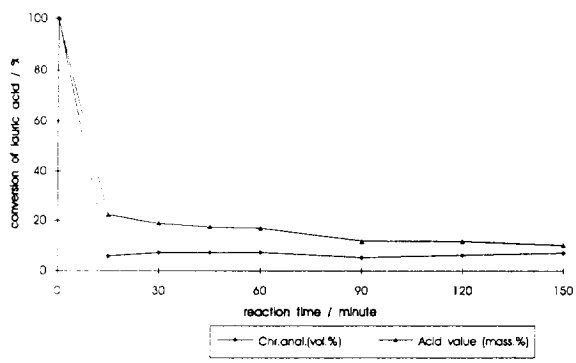

Fig. 5. Change in concentration of lauric acid reacted in the course of reaction with sorbitol at 160°C with previous cyclization of sorbitol with *p*-TSA as catalyst. ◆ = GC analysis (vol. %); ▲ = acid value (mass-%).

nation of the acid number (mass-%), demonstrating the quality of the sorbitol esterification reaction with lauric acid. It can be seen that the conversion was better when the sorbitol was previously cyclized (method B).

This work represents the solution to a real problem that should be of interest to surfactant and carbohydrate chemists. Workers in the food, cosmetic, detergents and general surfactants industries should also benefit from this work.

4. Conclusions

Trimethylsilyl derivatives of sorbitan fatty acid esters can be determined by GC. The conversion of lauric acid can be followed by GC analysis. The results of these analyses confirm the possibility of monitoring lauric acid and sorbitol esterification via the GC determination of lauric acid concentration.

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