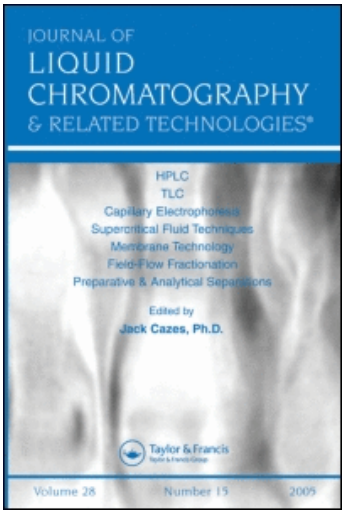

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Analysis of Sucrose Fatty Acid Esters Composition by HPLC

V. R. Kaufman[a]; N. Garti[a]
[a] Casali Institute of Applied Chemistry, School of Applied Science and Technology, The Hebrew University of Jerusalem, Jerusalem, ISRAEL

To cite this Article Kaufman, V. R. and Garti, N.(1981) 'Analysis of Sucrose Fatty Acid Esters Composition by HPLC', Journal of Liquid Chromatography & Related Technologies, 4: 7, 1195 — 1205
To link to this Article: DOI: 10.1080/01483918108068805
URL: http://dx.doi.org/10.1080/01483918108068805

JOURNAL OF LIQUID CHROMATOGRAPHY, 4(7), 1195-1205 (1981)

ANALYSIS OF SUCROSE FATTY ACID ESTERS COMPOSITION BY HPLC

V.R. Kaufman and N. Garti
Casali Institute of Applied Chemistry
School of Applied Science and Technology
The Hebrew University of Jerusalem
Jerusalem 91904, ISRAEL

ABSTRACT

Two procedures for quantitative analysis of sucrose fatty acid esters composition using HPLC are described. A reversed-phase column (RP-18) was used. The mobile phases consist of: a) methanol (95%) and isopropanol (5%); b) methanol (95%) and water (5%) using UV and RI detectors.

INTRODUCTION

Sucrose fatty acid esters are nonionic emulsifiers derived from transesterification reaction between sucrose and methyl fatty acid esters or fats (1).

Sucrose fatty acid esters are gaining an important role as food, cosmetic and pharmaceutical additives (2,3) because they proved to be non-toxic, tasteless, odorless and non-irritant, and they are available in wide range of HLB's (hydrophile-liphophile-balance), and have excellent emulsifying and dispersing abilities.

Sucrose fatty acid esters were obtained by many investigators in a variety of methods, which are all leading to a complex mixture of products. Due to the eight available positions for the transesterification reaction, many possible isomers of mono-, di- and poly sucrose esters can be formed. The commercial material is available as a crude mixture of products or as a partially purified white powder.

Since sucrose esters are used in food products it is important to evaluate their composition by simple, rapid and accurate methods. Only few investigators attempted to establish reliable and accurate methods for separation and analysis of the sucrose esters. The old technique, based on solvent extraction of sucrose monostearate and further purification by recrystallization (4), requires large samples and does not separate the isomers but just enriches the product with one of the isomers. Vioque and Holman (5) reported quantitative determination of the composition of sucrose esters mixtures by TLC. Mima and Kitamori (6) described an improved TLC method coupled with GLC, NMR and colorimetric determination of the product composition. An attempt to separate a commerical mixture of sucrose esters by HPLC was made by Cormier, Mai and Pommez (7) using one meter column packed with Fluoroether Sil-x-1 and a mixture of n-chloropropane and methanol as the eluent.

We have developed a procedure for a rapid and simple analysis of crude mixtures of sucrose esters using high performance liquid chromatography (HPLC) from which quantitative analysis of mono-, di-, tri- and the higher isomers can be accomplished. An alternative procedure has been developed for more detailed separation of mono- and di- isomers in the crude mixture. All the chromatograms were carried out using a simple RP-18 column and methanol, isopropanol and water as eluents.

MATERIALS AND METHODS

The chromatographic system consists of a SP-8000 high performance liquid chromatograph equipped with a UV SP-770 variable wavelength detector (Schoffel Instrument Corp.) and a Varian refractive index (RI) detector, fitted with a suitable prism (1.31 - 1.45 RI units).

The column was a commercially available 250 x 4.6 mm stainless steel packed with Lichrosorb RP-18 (10μ).

The mobile phases were: (a) Methanol (Baker analyzed Reagent) and isopropanol (for analysis, from Merck, Darmstadt, FRG) at a ratio of 95:5 (v/v). Solvents flow rate was 1.0 ml/min. Column temperature was 40°C and the pressure across the column was about 25 bars. (b) Methanol (Baker) and water (double distilled) 95:5 (v/v). Solvents flow rate was 1.0 ml/min. Column temperature was 55°C and the pressure across the column was about 25 bars.

The samples were dissolved in THF (Bio-Lab, HPLC grade) at 5-20 - wt%. The samples were: 1. commercial mixtures of sucrose stearate of Dai Ichi Kogyo Seiyabu Co. Ltd. with different amounts of mono-, di-, tri-, and poly-substituted esters of stearic (70%) and palmitic (30%) acids (F160, F140, F110, F90, F70 and F50). 2. Sucrose fatty acid esters of Talres Development Ltd. (Tal 20, Tal 21 and Tal 25), and 3. sucrose stearate and sucrose palmitate from the reaction in DMF (1).

Samples were injected automatically using a 10µl loop. The peaks were analyzed for area and percent by an inline SP-8000 data system. The instrument is equipped with sample withdrawal unit for further analysis by mass spectra (Du Pont 21-490 Low Resolution Single Focusing Mass Spectrometer) and TLC on Silica Gel G plates (Size 5 x 20 cm and thickness of 250µ; Fisher Scientific Co.) by the procedures used by Mima and Kitanori (6) and Cormier, Mai and Pommez (7).

RESULTS AND DISCUSSION

Since no pure reference materials exist, it was essential to identify the components of each mixture using other methods and also to rely partly on information given by the manufacturer.

Figure 1 demonstrates, in part, a typical chromatogram of sucrose esters mixtures claimed to contain 70% monoester (Figure 1.1) and 30% diester (Figure 1.2). The analysis was carried out using both UV detector (at 220 nm) and refractive index detector.

From Figure 1 and table I it can be seen that the chromatograms are quite similar for both detectors, and that there are only small differences in the percent composition.

The differences between the UV detector and the RI detector are due to the fact that the RI detector is less sensitive than the UV detector, and since each detector has different response for each component in the mixtures. The first three peaks are considered to be the monoesters summing to 71.2% monoester in F160 (The product contains 70% monoester according to the manufacturer data reports.) and 42.1% for F50 (30% are reported by the manufacturer.). These calculations are not accurate and nevertheless the amount of sucrose monoester is much smaller, because peak 1 was identified as methyl palmitate (by injection of authentic sample, to both HPLC, GLC and by mass spectrum analysis). Peak 2 consists

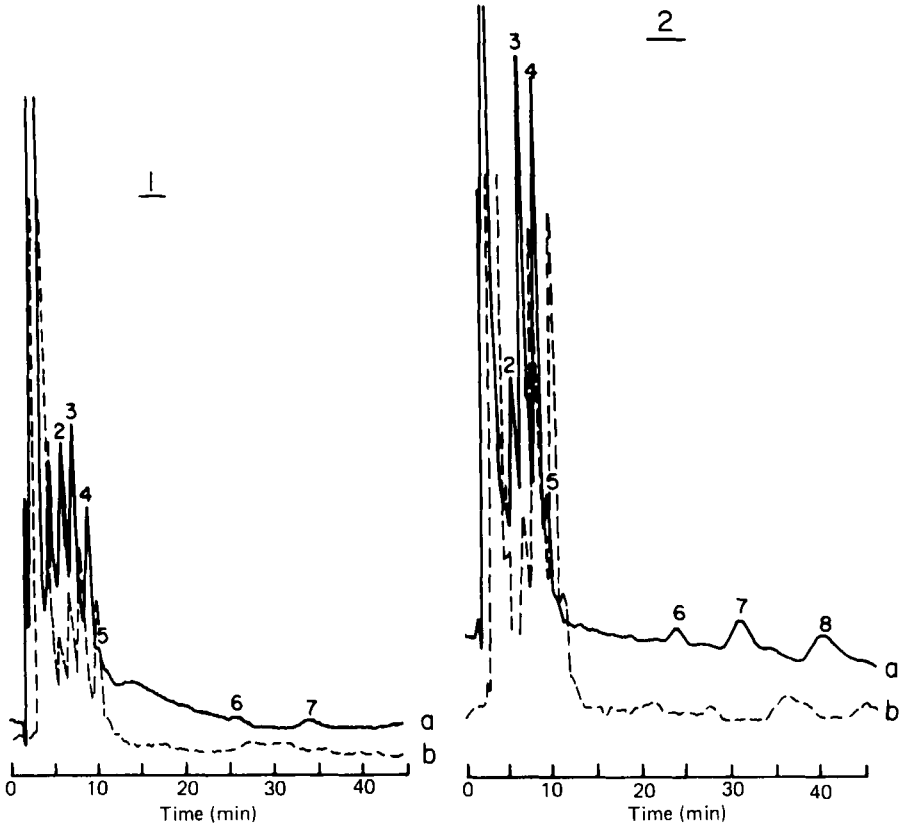

Figure 1: A typical chromatogram of commercial sucrose esters, from Dai Ichi Kogyo; F160 (70% monoester) (Figure 1.1) and F50 (30% monoester) (Figure 1.2)

Method a. Eluent: methanol and isopropanol 95:5 (v/v) 40°C
a. UV detector at 220 nm
b. RI detector

Peak 1 methylpalmitate; Peak 2 methylstearate and sucrose monopalmitate; Peak 3 sucrose monostearate; Peaks 4,5 sucrose diesters; Peak 6-8 sucrose polyesters

TABLE I

Summary of the Main Results Obtained from Separation of Two Commercial Sucrose Stearates Analyzed both by RI and UV Detectors. Retention Time Given in Minutes and Peaks in Percentage from Total Area.

Peak No.		(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
Retention time (min.)		5.1	6.1	7.1	9.2	10.2	20.4	26.5	30.1	35.1
F160	UV	6.1	27.5	37.6	22.05	2.14	0.36	1.0	0.5	2.6
	RI	10.7	29.2	38.1	13.2	8.6	----	----	----	----
F50	UV	0.3	11.2	30.5	32.8	5.8	----	3.1	6.5	0.2
	RI	1.1	12.8	45.9	39.0	1.0	----	----	----	----

of methylstearate and sucrose monopalmitate (as was proved by the above methods). The amount reported by the manufacturer is based on determination of hydroxyl values, saponification values and TLC analysis and these methods are subjected to considerable error, and are unable to distinguish between methyl esters and sucrose monoester. Therefore the manufacturer does not include the methyl esters among his products. Peaks 2 and 3 were identified as sucrose monoesters and 4 and 5 as diesters. The rest of the peaks are the polyesters.

The results for the other four samples (F140, F110, F90 and F70) which contain different amounts of the mono-, di and polyesters of sucrose were consistent with those obtained for the F160 and F50.

Figure 2 shows the chromatograms of sucrose fatty acid esters from Talres. Figure 2.1 shows the crude mixture of the transesterification product between sucrose and tallow fat (Tal 21). It can be seen that the chromatogram is similar to the chromatograms showed in Figure 1. The additional peaks at the beginning of the chromatogram (peaks 1-3) result from the tallow used for the reaction (authentic samples of tallow fat had the same retention time) which amounts to about 24%. Peaks 4 and 5 are the monoesters and sum up to about 30%. The other peaks are the di- and polyesters.

Figure 2.2 shows the crude mixture prepared by the tranesterification reaction between sucrose and methyl stearate-palmitate (Tal 25). Peaks

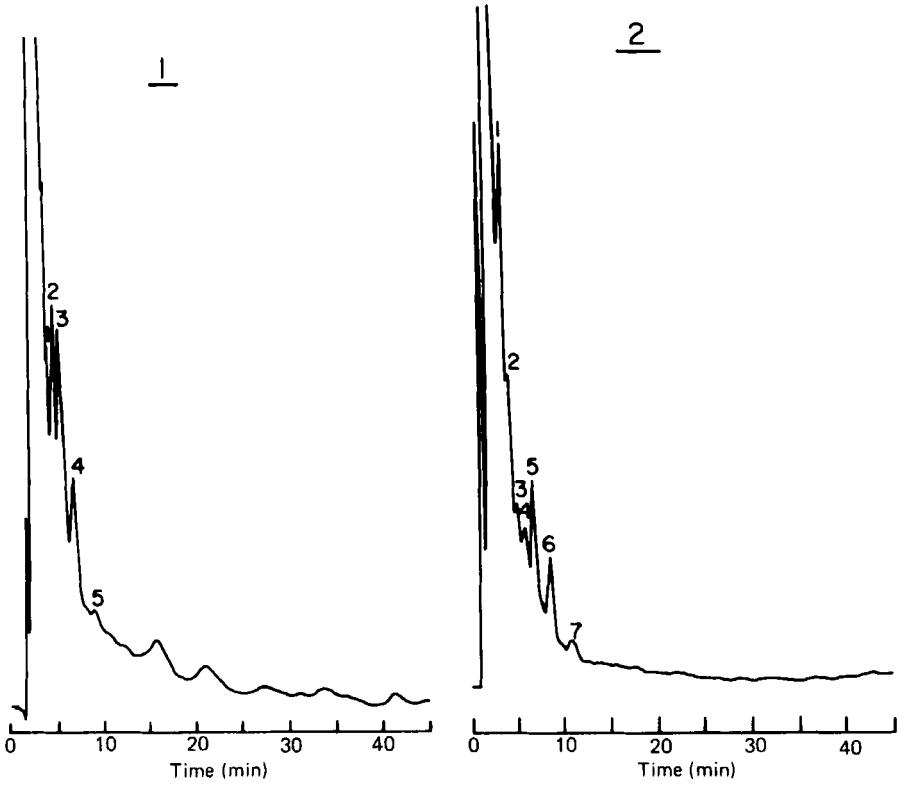

Figure 2: HPLC chromatogram of sucrose esters from Talers Dev. Tal 21 (Figure 2.1) and Tal 25 (Figure 2.2)

Method a. Eluent: methanol and isopropanol 95:5 (v/v) 40°C; UV detector at 220 nm. For Figure 2.1; Peaks 1-3 tallow; Peak 4 sucrose monostearate; Peak 5 sucrose distearate and for Figure 2.2; Peak 3 methylpalmitate; Peak 4 methylstearate; Peak 5 sucrose monostearate; Peaks 6-7 sucrose distearate.

1 and 2 belong most probably to the solvent used for the reaction. Peaks 3 and 4 are the methylpalmitate and methylstearate respectively, followed by peaks of the sucrose esters isomers which amount to about 61%.

The above chromatograms demonstrate a simple separation of sucrose esters from various sources with different compositions and in all cases

the separation is simple and it is easy to account for the amount of starting materials and the by-products in the sample.

Figure 3 shows the chromatograms of the crude products from the reactions in DMF, using separation method b. Figure 3.1 shows the HPLC chromatogram of the crude sucrose monopalmitate obtained from a reaction in which 99% methylpalmitate (Sigma Chemical Co.) was used. Peak 1 is derived from the DMF (used as the solvent). Peak 2 is the methylpalmitate left at the end of the reaction. Peaks 3-5 are possibly the three isomers of sucrose monopalmitate. Using the DMF transesterification process only small amounts of the higher isomers are formed and they are not detected by this method of separation, but their presence was proven by the first separation method.

Figure 3.2 shows the chromatogram of sucrose monostearate formed in DMF using 95% methylstearate (Aldrich). Due to prolonged reaction time, the amount of the mono isomers are smaller and the main product is sucrose distearate (peak 8). Peaks 2 and 3 are methylpalmitate and methylstearate respectively. Peaks 4-7 are sucrose monopalmitates and monostearates.

Figure 3.3 demonstrates a separation of the crude product obtained from a reaction between equal amounts of methylstearate and palmitate. Peaks 1-2 result from the use of DMF as the solvent for the reaction. Peaks 3 and 4 are methylpalmitate and methylstearate respectively. Peaks 5-10 are the sucrose monopalmitates and monostearates in good agreement with the results from Figures 3.1 and 3.2. Peaks 11 and 12 are the sucrose dipalmitate and distearate. The higher isomers are not formed in this reaction.

Figure 4 demonstrates the chromatograms of the sucrose ester mixtures F160 and F50, as analyzed by the second method. (For comparison see Figure 1.1 and 1.2.) The chromatograms show a much finer separation than by method a. Methylpalmitate and methylstearate are separated completely from the sucrose monopalmitate. Peaks 3-5 are the sucrose monopalmitate isomers, and peaks 6-8 are the sucrose monostearate isomers. Peaks 9 and 10 are dipalmitate and distearate respectively. Peaks 3-8 in Figure 4.1 sum up to 53.9% and in Figure 4.2 they sum up to 34.8%. This is in agreement with the manufacturer data indicating that F160 is richer in monoesters and F50 is richer in di- and polyesters. Peaks 11 and 12 are higher esters. Under these conditions it is not possible to identify the higher isomers.

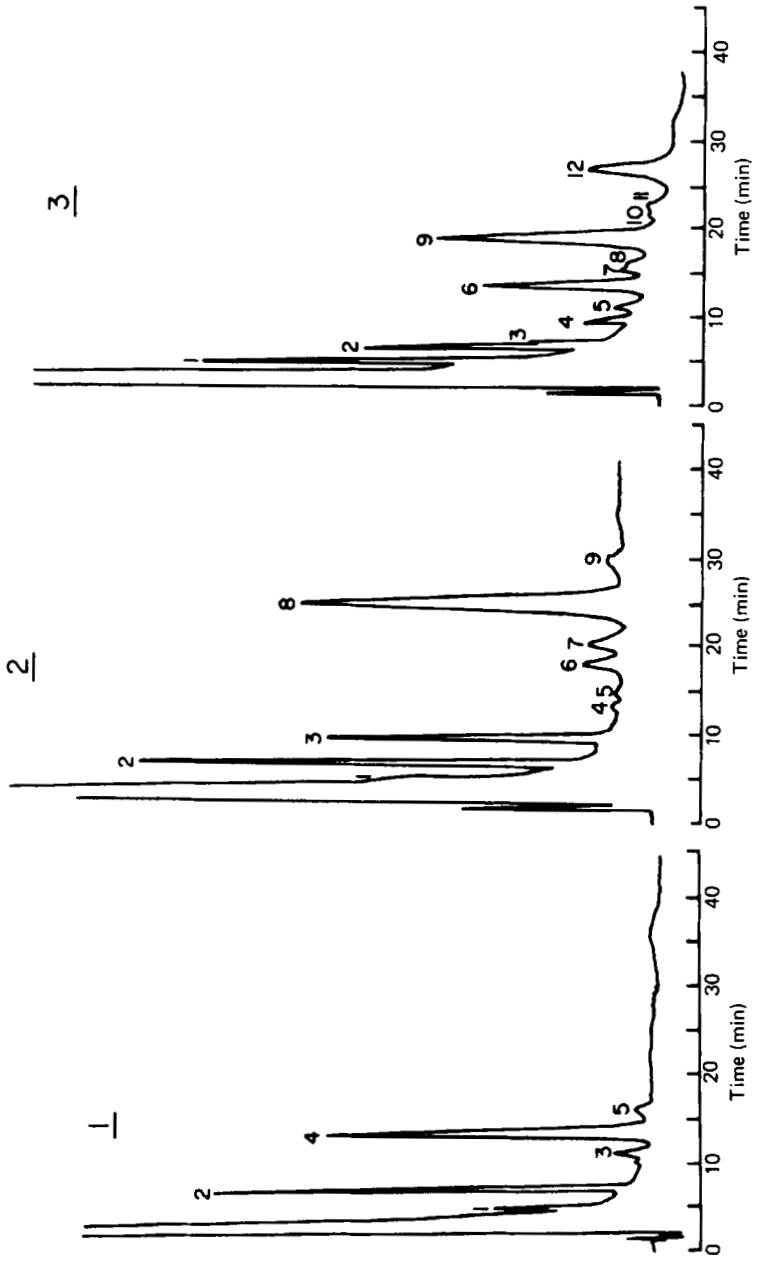

Figure 3: HPLC chromatogram of crude reaction mixture between methyl stearate and sucrose in DMF.

Method b. Eluent: methanol and H_2O 95:5 (v/v); 55°C
UV detector at 220 nm.

Sucrose palmitates (Figure 3.1), sucrose stearates (Figure 3.2) and sucrose monopalmitate and monostearate mixture (Figure 3.3)

Figure 3.1: Peak 2 methylpalmitate; Peak 3-5 sucrose monopalmitate isomers

Figure 3.2: Peak 2 methylpalmitate; Peak 3 methylstearate; Peaks 4-5 sucrose monopalmitate and 6-7 sucrose monostearate isomers

Figure 3.3: Peak 3 methylpalmitate; Peak 4 methylstearate; Peaks 5-7 sucrose monopalmitate and 8-10 sucrose monostearate isomers; Peak 11 sucrose dipalmitate; Peak 12 sucrose distearate.

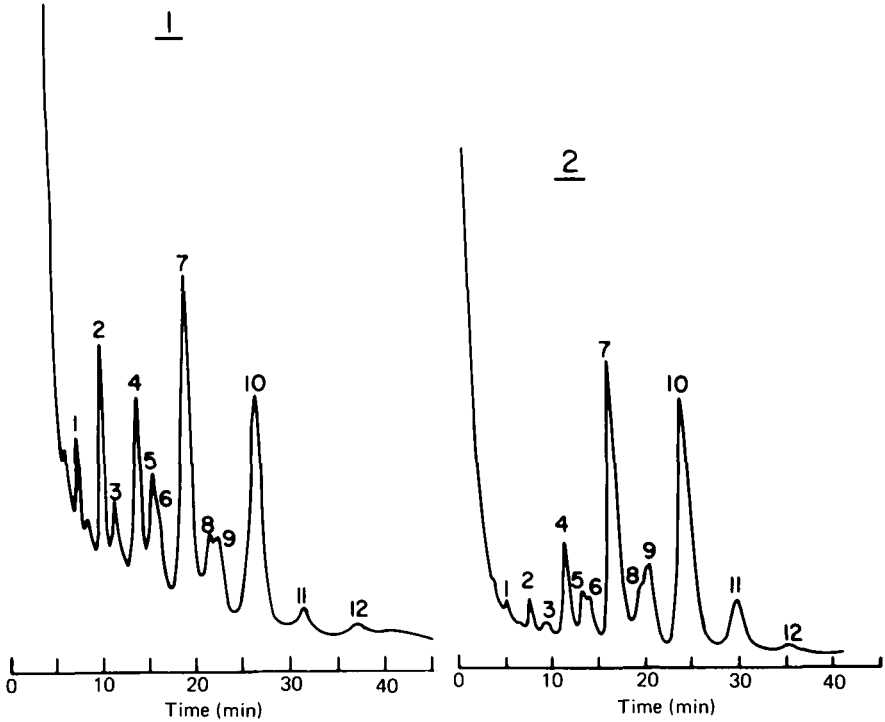

Figure 4: HPLC chromatogram of commercial sucrose esters Dai Ichi Ichi Kogyo Seiyabu F160 (Figure 4.1) and F50 (Figure 4.2)

Method b. Eluent: Methanol and H_2O 95:5 (v/v); 55°C; UV detector at 220 nm.

Peak 1 methylpalmitate; Peak 2 methylstearate; Peaks 3-5 sucrose monopalmitate; Peaks 6-8 sucrose monostearate; Peak 9 sucrose dipalmitate; Peak 10 sucrose distearate; Peaks 11-12 sucrose polyesters.

Similar chromatograms were obtained for other samples of this series of products.

CONCLUSIONS

Sucrose esters are usually a complex mixture of isomers. A need for analyses of these emulsifiers may arise at several stages of their

production and use such as production control and detection of batch-to-batch variations, and for comparison of emulsifiers purchased from different suppliers, and, finally, upon requirements of authorities regulations.

The HPLC technique can serves as a simple and accurate method for separation and determination of the product composition of any crude product mixture.

ACKNOWLEDGEMENT

The authors wish to express their gratitutde to Professor Eli Grushka from the Analytical Department of the Hebrew University of Jerusalem for his helpful comments.

The support of the Robert Szold Research Foundation is gratefully acknowledged.

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