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SYNTHESIS AND PROPERTIES OF SUCROSE POLYESTERS OF SAFFLOWER OIL FATTY ACIDS

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ABSTRACT: Sucrose polyesters (SPE) were synthesized by interesterification of sucrose and long chain fatty acid methyl esters of safflower oil. A typical synthesis required: reaction time of 11.5h, synthetic temperature 144 ± 0.5°C, substrate molar ratio of 11.4:1 (fatty acid methyl esters : sucrose). Sucrose polyesters confirmed by infrared (IR) and H^1- nuclear magnetic resonance (H^1– NMR) spectroscopy. Physical properties of sucrose polyesters were similar to that of its conventional oil.

Key words: Safflower, sucrose, polyesters, fatty acids, methyl esters, esterification.

INTRODUCTION

Sucrose polyesters (Olestra) uses in foods as reduced or zero calorie fat and oil substitutes has already been brought to consumers attention by the food industry (Akoh and Swanson 1990). Sucrose polyesters (SPE) consists of mixture of hexa-, hepta-, and octaesters, formed by reaction of sucrose with long chain fatty acids by interesterification. (Mattson *et al.*, 1971, Weiss *et al.*, 1972 and Bobalek, 1977). Sucrose polyesters having a degree of substitution (D.S.) of 5-8 can be prepared by the solvent-free interesterification process of Feuge *et al.* (1970) involving molten sucrose and fatty acid methyl esters (FAME) of long chain fatty acids catalyzed by lithium, sodium or potassium soaps. Direct esterification of sucrose with fatty acids is limited by the tendency of sucrose to caramelize at temperature greater than 185°C. A solvent-free two-step reaction process was described by Rizzi and Taylor (1976 and 1978) in a

effort to avoid toxic solvents. Mieth *et al.* (1983) reported that yield of 80 – 90% SPE of homogenous fatty acid composition by reacting sucrose octaacetate and methyl palmitate in the presence of Na or K metal. Volpenhein (1985) improved the solvent free process for SPE production. Akoh and Swanson (1990) reported a optimized synthesis of SPE that gave yields between 99.6 – 99.8% of the purified SPE based on the initial weight of sucrose octaacetate (SOAC). Boutte and Swanson (1994) modified the soap method using a rotary evaporator in a laboratory scale experiment. Megahed (1999) used a simple method for preparation of SPE from FAME in the absence of any organic solvent. Jandacek and Webb (1978) reported the physical properties of completely esterified SPE synthesized with a single or homogenous fatty acids. The physical properties of SPE have been reported by Hamm (1984) and Akoh and Swanson (1990). Physical properties of SPE can be adjusted by varying the degree of unsaturation and chain length of the fatty acids used in the synthesis to produce SPE with functional properties appropriate for food use, (Akoh and Swanson 1990). Fouad *et al.* (2001) reported that SPE has physical properties similar to triacylglycerols except resistant to lipolysis, and thus proposed as a zero-calorie fat substitute.

The objective of this study was to optimize the conditions for synthesis of safflower sucrose polyesters (SPE) from fatty acid methyl ester (FAME) of safflower oil and to compare the physical properties of the synthesized SPE with that of safflower oil.

MATERIALS AND METHODS

Materials

Pure safflower oil was extracted from safflower seeds of Giza 1 obtained from Giza Research station, Agriculture Research centre, Department of oil crops. Sucrose, sodium hydroxide potassium carbonate, potassium hydroxide methanol, ethanol, hydrochloric acid, acetic acid, petroleum ether, diethyl ether, silica gel for column and for TLC were purchased from EL-Nasr pharmaceutical chemicals company (ADWIC). Tonsil 550-FF bleaching clay was obtained from Arma Food Industries Co. At 10th of Ramadan City, Egypt.

Methods

Preparation of Fatty Acid Methyl Esters (FAME)

Fatty acid methyl esters (FAME) of safflower oil were prepared according to the method of Akoh and Swanson (1988).

Synthesis of Safflower Oil Sucrose Polyesters (SPE)

SPE was prepared according to the method of Boutte and Swanson (1994) and modified by Shieh *et al.* (1996).

Purification of SPE

SPE was purified according to the method of Riose *et al.* (1994).Thin-layer chromatographic (TLC) method described by Malins and Mangold (1960) was used for detection of purification process.

Physical Properties of SPE

Viscosity was measured with an Ostwald viscosity pipette method at 20°C and values are expressed in centipoise (cp). Refractive index (RI) measured by Zeiss refractometer and specific gravity (Sp gr.) were determined according to the methods reported by A.O.A. C (1990).

The colour of sample was determined according to (A. O. C. S 1985). A lovibond tintometer model (E) was applied to measure the colour using 5.25 inch cell.

Structure Confirmation of Safflower SPE

Infra-red absorption spectra (IR)

SPE sample was dissolved in few drops of chloroform and the resultant solute was used to saturate KBr tablets which were subsequently inserted in 0.1 mm NaCl cells to be finally analysed using Jasco 460 FTIR spectrometer (Jasco, Japan)

Proton-nuclear magnetic resonance (H^1-NMR)

H^1-NMR spectra was performed using a Varian Gemmini 200 spectrometer operating at 200 MHZ and equipped with an internal 6.26 KHZ deuterium lock. A known amount of SPE (1 mg) was dissolved in 1 ml of deuterated chloroform ($CDCl_3$) containing 2.5 mg of 3-(trimethylsilyl) propane sulfuric acid sodium salt. However, when analyzing sucrose, deuterated dimethyl sulfoxide (DMSO) was used instead of $CDCl_3$ and the analysis was conducted under the same conditions as for the SPE analysis.

RESULTS AND DISCUSSION

The structure of sucrose polyesters (SPE or Olestra) synthesized by esterification between sucrose and long chain fatty acid methyl esters is shown in Fig. (1). The degree of substitution (DS) is defined as the number of hydroxyl groups esterified with long chain fatty acids.

Purification process by means of silica gel column chromatography was conducted and the pure SPE mixture was obtained.

Physical Properties of SPE

The data of the physical properties of safflower SPE were nearly similar to that of safflower oil (Table 1). The SPE is liquid at room temperature (ca. 22°C). In this respect, Akoh and Swanson (1990) outlined that the carbohydrate polyesters must contain at least half unsaturated fatty acids to be liquid at ambient temperature. The refractive index (R.I) of SPE was 1.4721 slightly higher than that of safflower oil (1.4671). These data are similar to the findings of Akoh and Swanson (1990) and Shieh *et al.* (1996).

The specific gravity (Sp. gr.) of SPE (0.930) was slightly higher than that of safflower oil (0.9228). These data agreed with findings of Akoh and Swanson (1990) and Shieh *et al.* (1996).

Over all, the R.I., and Sp. gr. values of SPE were increased with the increase in the degree of unsaturation. The refractive index of liquid SPE was comparable to that of liquid sucrose octaesters as reported by Jandacek and Webb (1978). Viscosity of SPE (142) was slightly higher than the viscosity of safflower oil (140). This result is similar to that of Jandacek and Webb (1978), Akoh and Swanson (1990) and Shieh *et al.* (1996). The color of SPE was pale yellow which was similar to the color of safflower oil. This result is similar to Akoh and Swanson (1990) data.

Table 1: Physical properties of safflower oil and its sucrose polyesters

	Refractive index at 40°C	Specific gravity at 20 °C	Viscosity at 20°C (cp)	Color
Safflower SPE	1.4721	0.930	142	Pale yellow
Safflower oil	1.4674	0.9228	140	Pale yellow

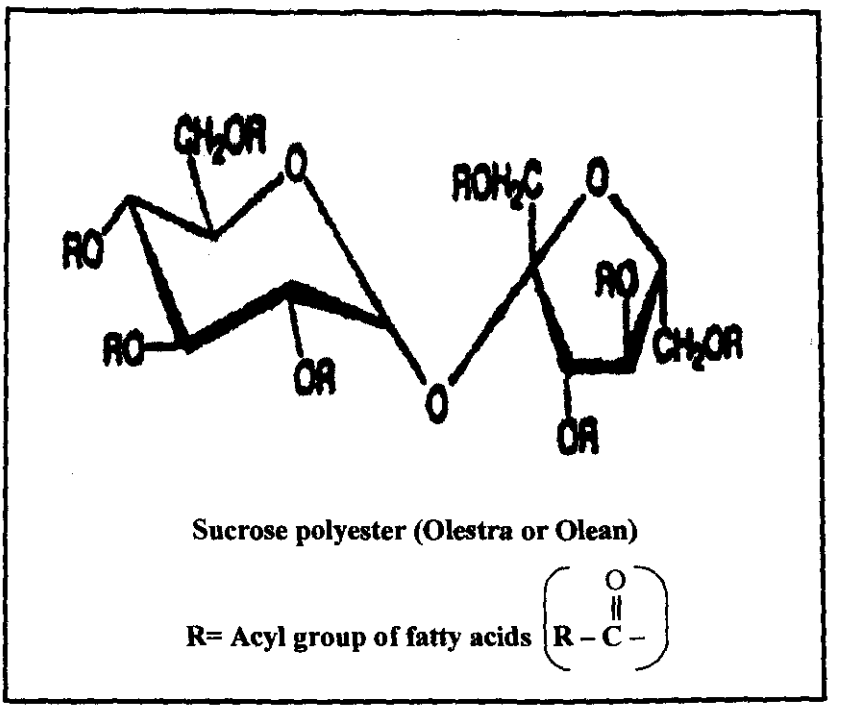

Fig. 1: Structure of sucrose polyester (olestra)

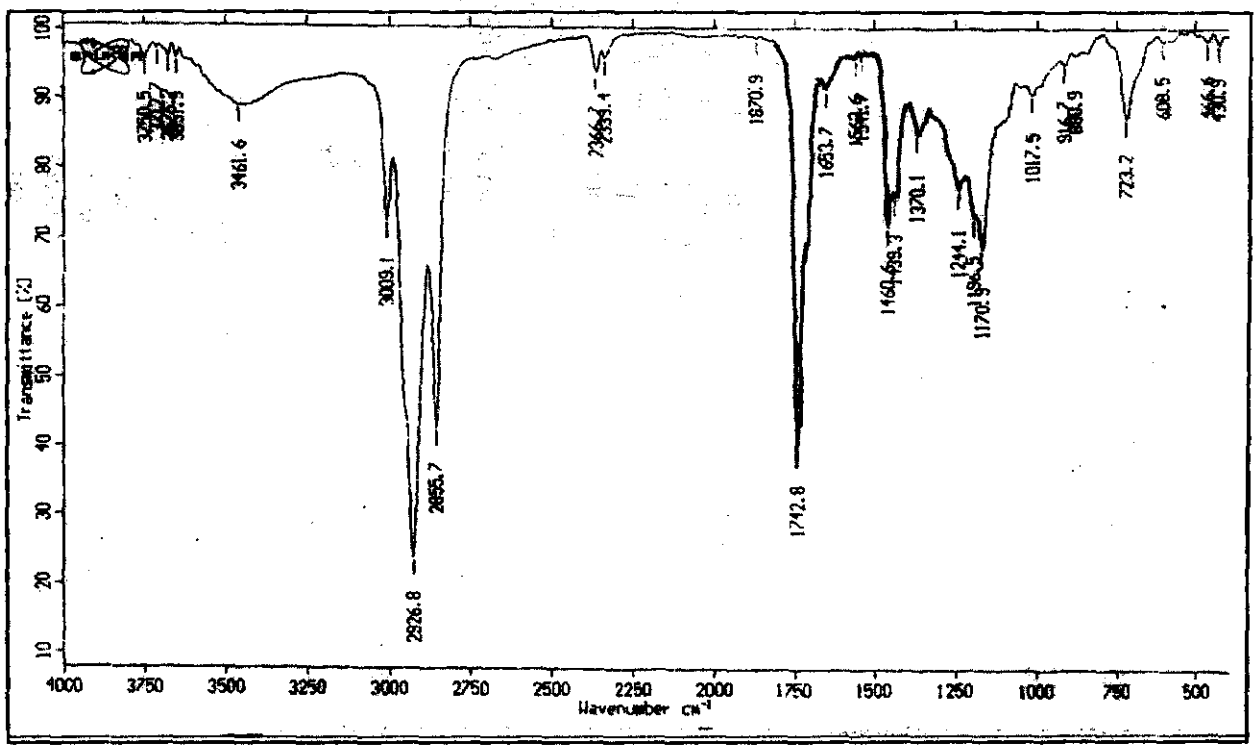

Fig. 2: Infra red spectrum of safflower oil sucrose polyesters

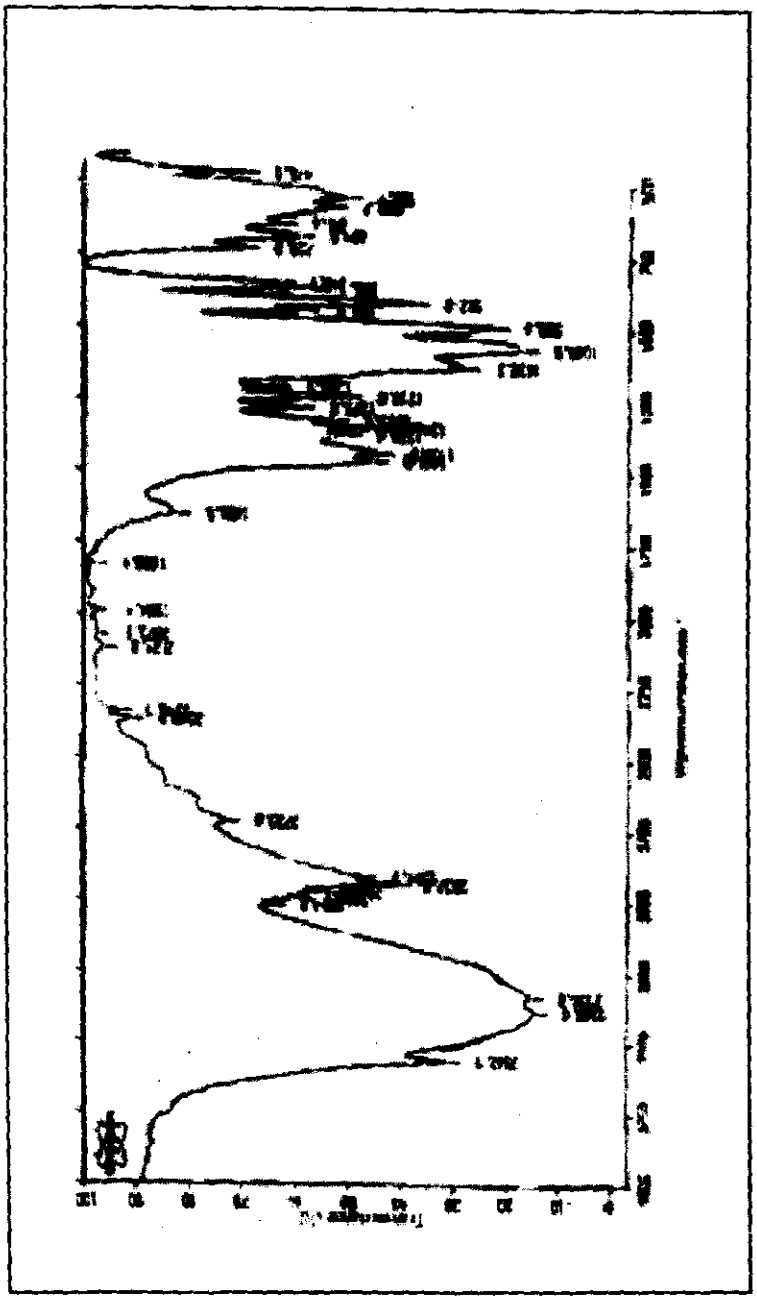

Fig. 3: Infra red spectrum of sucrose

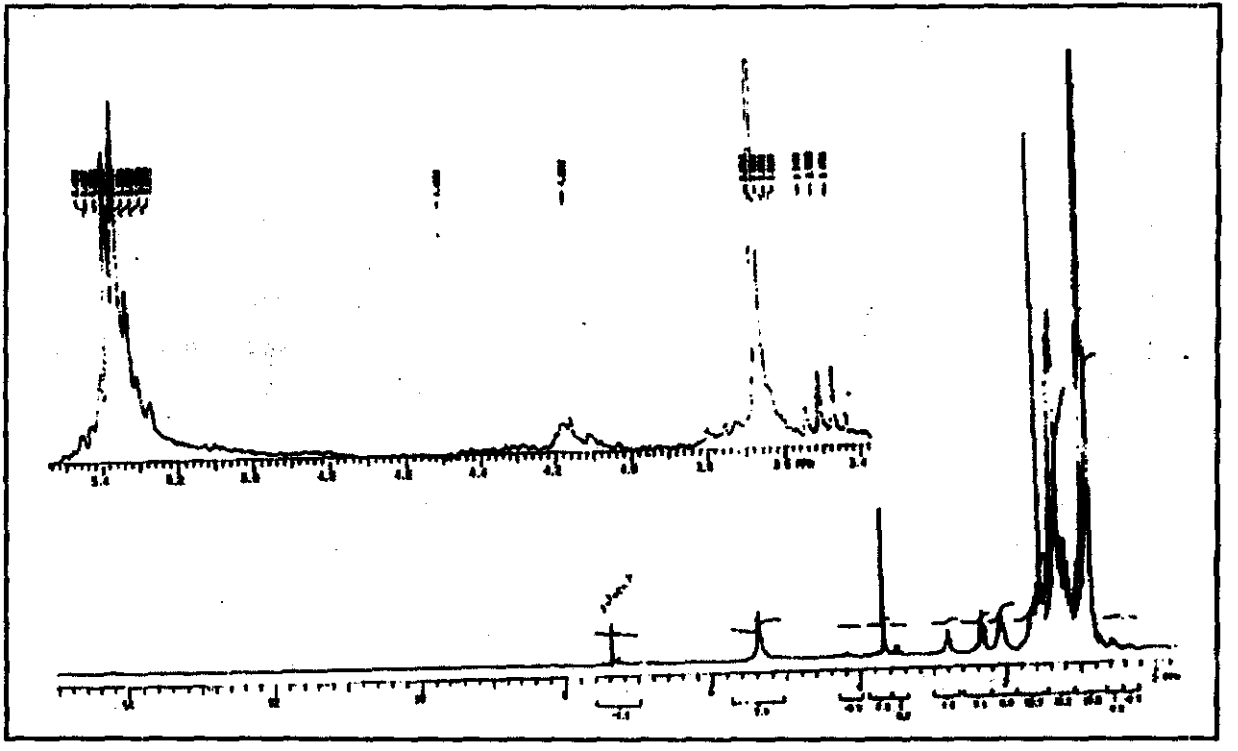

Fig. 4: H^1-nuclear megnetic resonance spectrum of safflower oil sucrose polyesters

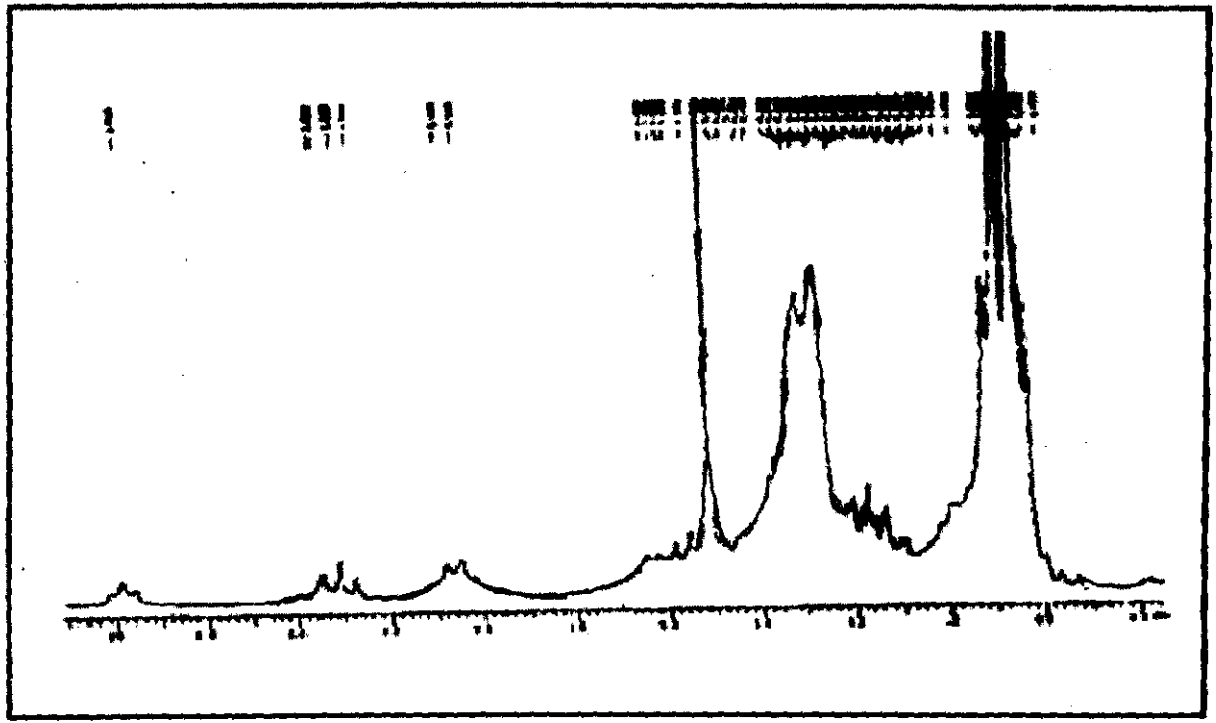

Fig. 5:H^1- nuclear megnetic resonance spectrum of safflower oil sucrose polyesters

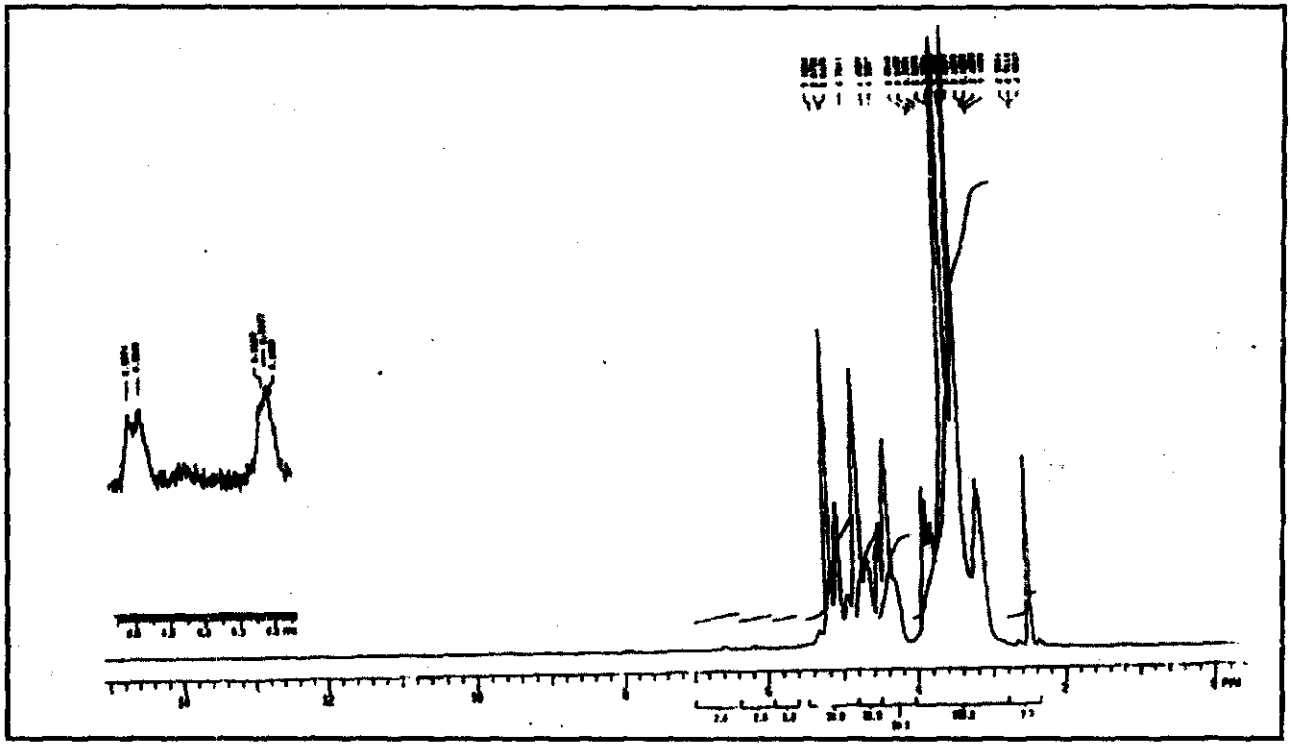

Fig. 6: H^1-nuclear megnetic resonance spectrum of sucrose

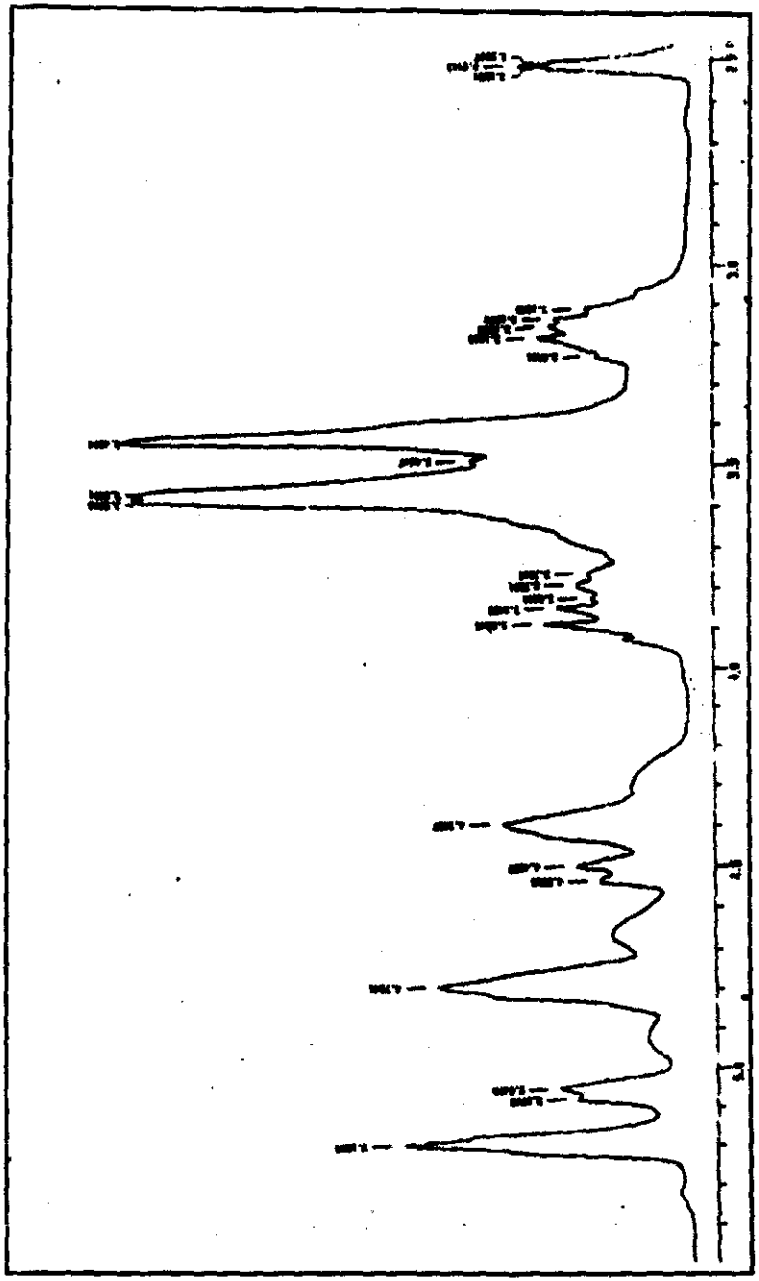

Fig. 7: H^1-nuclear megnetic resonance spectrum of sucrose

Structure Confirmation of Safflower SPE

Infra red (IR), proton NMR (H^1- NMR) spectroscopy have been routinely used to elucidate the structure of the synthesized safflower oil sucrose polyesters. Spectral data of SPE synthesized from mixed fatty acids seems to be not previously reported.

The IR Spectra of Liquid Safflower Oil and its SPE

In the IR spectrum of SPE (Fig. 2), asymmetrical stretching and stretching vibrations of the methyl and methylene groups of the fatty acid chains were observed in the region of 3000 – 2860 cm^{-1}. However, an absorption band at 1740 cm^{-1} by ester carbonyls in the IR spectrum of SPE was absent in the IR spectrum of sucrose (Fig. 3). This indicates that the fatty acid chains present in SPE are esterified to sucrose. An absorption band of the hydroxyl group at 3335cm^{-1} in the IR spectrum of sucrose (Fig.3) was not present in the IR spectrum of SPE (Fig. 2). This indicates that all hydroxyl groups in sucrose were esterified. Our data were similar to that reported by Akoh and Swanson (1987 and 1990).

H^1- NMR Spectra of Safflower SPE

H^1 -NMR spectra of SPE and sucrose, are shown in Figures (4, 5, 6 and 7 respectively). Signals of methyl group on the omega end of fatty acid chains, methylene group of fatty acid chains and methine group connected to a double – bonded carbon protons were located at 0.799-0.826,1.201-1.226 and 1.933-1.945, respectively. Signals from the protons of hydroxyl groups were observed at 4.2 – 4.7 ppm in the spectrum of sucrose but were not observed in the spectrum of SPE. These results show that the fatty acids were esterified to sucrose molecules and the free hydroxyl groups are not present in SPE molecules. Our data are similar to that of Chung *et al.* (1996).

Both the IR and H^1 NMR data indicate that SPE was successfully synthesized by intersterification.

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التخليق والخصائص لاستر السكروز العديد للأحماض الدهنية لزيت القرطم

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يؤدى الإفراط فى تناول كميات كبيرة من الزيوت والدهون إلى زيادة وزن الجسم ويصاحب ذلك الإصابة بالعديد من الأمراض مثل السمنة وتصلب الشرايين وغيرها، لذلك فإن تقليل مستوى الدهن فى الغذاء تم عن طريق استخدام بعض البدائل التى لها نفس الخواص الطبيعية للزيوت والدهون ولكنها منخفضة فى محتواها من الطاقة، ومن هذه البدائل السكروز عديد الاستر المنتج من زيت القرطم.

تم تكوين استرات الميثيل للأحماض الدهنية من زيت القرطم، ثم استخدمت هذه الاسترات مع سكر السكروز بهدف إنتاج مركب السكروز عديد الاستر واستخدمت أجهزة الامتصاص فى منطقة الأشعة تحت الحمراء والتردد النووى المغناطيسى للتأكد من حدوث عملية الأسترة الكاملة.

تمت دراسة الخواص الطبيعية للسكروز عديد الاستر ومقارنتها بالخواص الطبيعية لزيت القرطم بدراسة اللون ومعامل الانكسار واللزوجة والكثافة النوعية حيث كان لون المركب الناتج للسكروز عديد الاستر هو نفس لون زيت القرطم الأصلى. إرتفاع طفيف فى قيم معامل الإنكسار والكثافة النوعية واللزوجة للسكروز عديد الإستر عن مثيليتها فى زيت القرطم الأصلى.

حيث كانت النتائج كالآتى :

- معامل الإنكسار للسكروز عديد الاستر ١,٤٧٢١ بينما لزيت القرطم الأصلى كان ١,٤٦٧٤.
- الكثافة النوعية عند درجة حرارة ٢٠°م للسكروز عديد الإستر كانت ٠,٩٣٠ بينما كانت للزيت الأصلى ٠,٩٢٢٨ .
- اللزوجة عند درجة حرارة ٢٠°م للسكروز عديد الاستر كانت ١٤٢ بينما كانت للزيت الأصلى. ١٤٠.