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Surface Activity of Glycerol Glycoside Palmitates

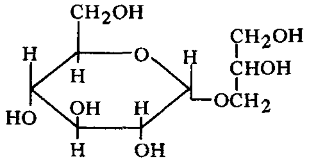
ABSTRACT

A glycoside ester product was prepared by the transglycosylation of starch and glycerol, which yielded a mixture of 2,3-dihydroxypropyl-α-D-glucopyranoside and other glycerol glycosides, followed by interesterification of the crude glycerol glycosides with a mixture of mono-, di- and tripalmitin. The purified reaction product, consisting of ca. 77% glycerol glycoside palmitates, 14% palmitins and 9% free palmitic acid, was found to be extremely effective in lowering the interfacial tension between cottonseed oil and water—a 0.04% concentration in the oil phase lowering the interfacial tension to 1.3 dynes/cm.

Fatty acid esters of the glycerol glycosides occur naturally (1-3), and a patent application has been filed on the use of certain glycoside esters as emulsifiers in foods (4). However reports on the physical properties of such compounds are practically nonexistent. We wish to report on the exceptionally high surface activity found for one type of product.

A number of glycerol glycoside ester products have been prepared and examined by us, but the preparation and characteristics of only one of the products will be reported at this time.

This product, a mixture of glycerol glycoside palmitates, was prepared by a "one pot" procedure. Into a glass reaction flask equipped with a mechanical stirrer there was placed 276.3 g (3.00 moles) anhydrous glycerol and 1.45 g (0.33%, based on the glycerol and starch to be used) of sulfuric acid. The free space in the flask was flooded with nitrogen, the stirrer was started, and the flask and contents were heated to 125 C. While the contents of the flask were kept at 125 C, under nitrogen, and with the stirrer working, 162.14 g (1.00 equivalent of an anhydroglucose unit) of anhydrous, waxy cornstarch was added in the course of 20 min. The reaction was continued for an additional 60 min at 125 C to convert the starch into glycerol glycosides. To this point the procedure is essentially that of Otey et al. (5), which has been shown to yield a mixture of glycosides, including 2,3-dihydroxypropyl-α-D-glucopyranoside,



and its β-anomer.

TABLE I

Properties of the Glycoside Ester Fraction

Property	Value
Glycoside esters	76.9%
Palmitins	
Mono-	4.2%
Di-	6.1%
Tri-	4.0%
Palmitic acid	8.8%
Hydroxyl value	250
Melting point	59 C

The reaction flask and its content of glycerol and glycerol glycosides were cooled to ca. 90 C, and 1.564 g sodium carbonate was added slowly to neutralize the sulfuric acid. Sodium palmitate in the amount of 33.10 g (5%, based on the weights of glycerol glycosides, glycerol and the mixed palmitins to be used) was added. Then 223.5 g of mixed palmitins (ca. 60% di-, 22% mono- and 17% tripalmitin) containing 0.75 equivalent of palmitic acid was added.

With the mechanical stirrer working, the head space of the reaction flask again was flooded with nitrogen, and the reactants were heated to and kept at 190 C for 20 min. Glycerol then was removed by vacuum distillation over a period of 80 min, during which time the pressure dropped to 2-3 mm of mercury.

The crude reaction product, a brittle, tan-colored solid, weighed 464.0 g. The product was dispersed in an ethyl acetate-water mixture and washed first with a saline solution containing 0.67 mole orthophosphoric acid per mole of soap, then with a saline solution and finally with water. The glycoside ester fraction, which was found by analysis to be free of soap and unreacted glycosides, amounted to 56.8% of the crude reaction product. Other analytical data on the glycoside ester fraction revealed the properties shown in Table I.

Portions of the glycoside ester fraction were added to cottonseed oil, which had been passed through a silicic acid column to remove any residual soaps; and the interfacial tension of the cottonseed oil solution against water was measured at 70 C with a Cenco-du Nouy interfacial tensiometer. The results are shown in Table II.

The glycoside ester fraction was ca. 130 times more effective than monopalmitin (6) in reducing the interfacial tension between cottonseed oil and water to one-half its original value. Indeed the glycoside ester fraction apparently was even more effective than the ordinary soaps,

TABLE II

Effect of Glycoside Ester Fraction on Interfacial Tension between Cottonseed Oil and Water

Concentration of glycoside ester fraction in oil, %	Interfacial tension, dynes/cm
0.00	29.4
0.01	14.5
0.02	6.8
0.03	3.7
0.04	1.3

which are claimed to lower the interfacial tension between water and glyceride oils to 2-5 dynes/cm when present in the amount of 0.1% (7).

It would appear that glycoside ester products of the type described are potentially useful as surface active agents in a number of food and nonfood products. As one example, these glycoside esters which are closely related to the glycolipids of wheat flour (1), may be as effective as the glycolipids of wheat flour in improving the quality of high protein breads (8).

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Gas Chromatograms of Synthetic Liquid Waxes Prepared from Seed Triglycerides of Limnanthes, Crambe and Lunaria

ABSTRACT

Compositions of synthetic liquid waxes derived from erucic-containing seed oils vary considerably. These differences, when determined by gas chromatography, allow "fingerprint" identification of the source of oil.

The synthesis and physicochemical evaluation of liquid wax esters derived from erucic-containing triglyceride oils, which were extracted from seeds of *Limnanthes douglasii*, *Crambe abyssinica* and *Lunaria annua*, were reported earlier (1,2). The gas liquid chromatographic (GLC) procedure developed recently (3) for the compositional analysis of the natural liquid wax ester from *Simmondsia californica* (Jojoba) has now been applied to these synthetic wax esters. Although these products have physical properties similar to jojoba oil, they are quite distinct in their chemical composition. Differences become apparent and identification is simplified when gas chromatograms of the oils are compared in fingerprint fashion (Fig. 1). The area per cent of each component in the oil is shown in Table I.

As expected, the composition of the synthetic liquid wax esters coincided with the calculated composition for a random combination of the fatty alcohol mixture with the mixture of fatty acids from the parent triglyceride oil. The calculated weight percentages are given in parentheses. Jojoba showed a nonrandom combination of its acids and alcohols; the preferential esterification of docosenol to eicosenoic acid implies that, at a certain stage of jojoba seed development, docosenyl eicosenoate is biosynthesized almost exclusively (3).

GLC experimental conditions were: high temperature silicone liquid-phase OV-1, 3% on Gas Chrom Q, acid-washed, silylated, 100-120 mesh; stainless steel column, 0.2 cm ID, 0.3 cm OD, 100 cm long; helium carrier gas, 100 ml/min, 100 psig; programing rate 2 C/min; injection port 350 C, on column; flame ionization detector oven 385 C.

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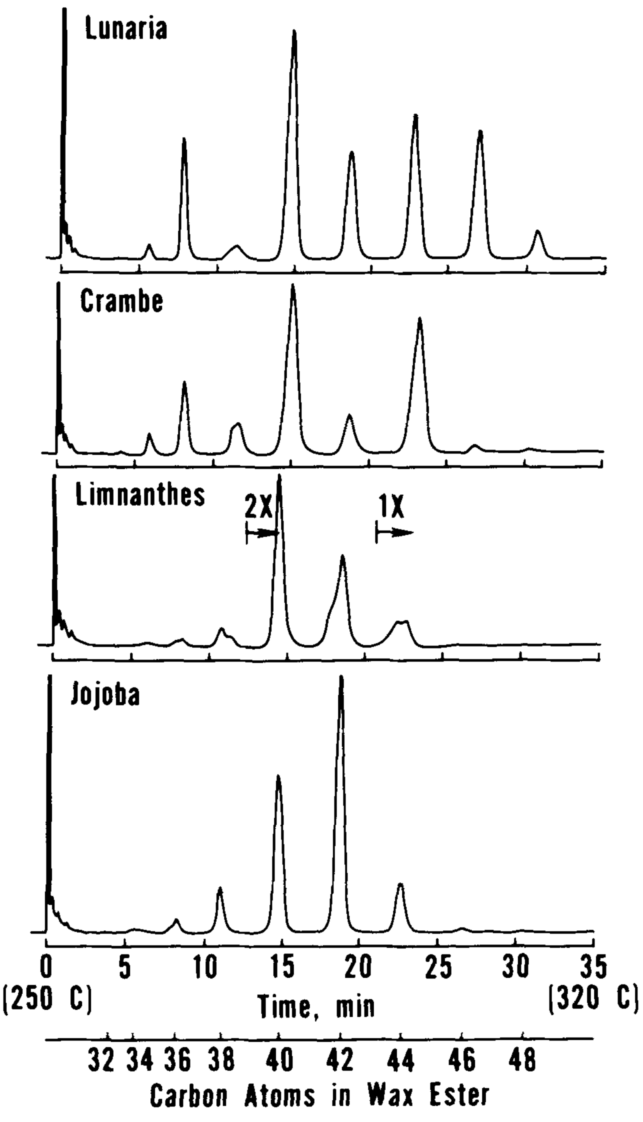

FIG. 1. Gas chromatograms of synthetic liquid waxes prepared from seed triglycerides of *Lunaria annua*, *Crambe abyssinica* and *Limnanthes douglasii* and of natural liquid wax extracted from jojoba nuts. Experimental conditions are detailed in the text.

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