Synthesis and Properties of Alkyl Glycoside and Stachyose Fatty Acid Polyesters

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A solvent-free interesterification procedure was used to synthesize alkyl glycoside fatty acid polyesters: methyl glucoside polyesters, methyl galactoside polyesters, octyl glucoside polyesters, and tetrasaccharide fatty acid polyester, stachyose polyester. To obtain high yields, the hydroxyl groups on alkyl glycosides and stachyose were first protected by acetylation, and thereafter interesterified with fatty acid methyl esters (FAME) of long chain fatty acids to yield saccharide polyesters.

Spectral analysis indicated excellent substitution of fatty acids onto the saccharide moiety. Quantitative C-13 NMR spectroscopic data calculation of the degree of substitution on the saccharide acetates and the saccharide fatty acid polyesters were obtained using chromium acetyl acetonate. Studies of the physical properties of the polyesters indicated that the alkyl glycosides and stachyose polyesters were not markedly different from sucrose polyesters (SPE) or triglycerides. *In vitro* lipolysis indicated no evidence of hydrolysis, suggesting potential use of alkyl glycoside and stachyose fatty acid polyesters as low calorie oils.

During the synthesis of sugar fatty acid polyesters, direct esterification of the reducing sugars such as glucose and galactose resulted in excessive sugar degradation and charring. The use of non-reducing sugar acetates for the synthesis of saccharide polyesters has been reported previously (1-4). Linstead *et al.* (5) described complete acetylation of sucrose to sucrose octaacetate. Sugar acetates exhibit lower melting points compared to the free sugar and are particularly useful in the synthesis of sugar polyesters at reduced temperatures (2).

Preparation of alkyl glycosides generally involves reacting a sugar with alcohol in the presence of acid catalysts (6). Glycosylation is necessary to convert reducing sugars with reactive C-1 anomeric centers to non-reducing, less reactive anomeric centers. Synthesis of alkyl glycoside as solubilizing agent for membrane proteins (6), methyl glucoside fatty acid esters as emulsifiers (7,8), and sugar glycoside fatty acid esters as additives to culinary mixes have been reported previously (9). Gibbons and Swanson (7) reported direct esterification of one mole of methyl glucoside with two moles of free fatty acids in the presence of lead or stannous soap catalysts to produce methyl glucoside diesters with half the methyl glucoside remaining unreacted. Albano-Garcia *et al.* (8) reported a solventless synthesis of methyl glucoside esters of coconut fatty acids in the presence of 5% anhydrous potassium soap as catalyst and temperatures of 145-148°C.

Little has been reported on the synthesis of methyl glucoside fatty acid polyesters of glucose, galactose or octyl glucoside fatty acid polyesters. Alkyl glycoside polyesters may be an innovative possible low calorie oil replacement of conventional edible oils. The potential for successful synthesis, application and consumption of alkyl glycoside polyesters as non-caloric fat substitutes appears to be great.

The possibility of synthesizing larger saccharide fatty acid polyesters such as stachyose and verbascose polyesters was demonstrated by the successful synthesis of raffinose fatty acid polyesters (2). Stachyose is a non-reducing heterogenous sugar similar to raffinose, except that stachyose (Gal-Gal-Glu-Fru) contains one more galactose unit.

Analyses of carbohydrate fatty acid polyesters by C-13 NMR spectroscopy has been suggested as a potential tool for determining the degree of substitution (2). High pressure gel permeation chromatography has been used to analyze sucrose polyesters in feces and diets (10,11).

The objectives of this investigation were to synthesize alkyl glycoside fatty acid polyesters and stachyose fatty acid polyesters by a one-stage solvent-free interesterification process utilizing alkyl glycoside and stachyose acetates as starting materials, to extend the use of C-13 NMR spectroscopy as an analytical tool in determining degree of substitution (D.S.) and to demonstrate the potential use of alkyl glycoside and stachyose fatty acid polyesters as low calorie oils.

MATERIALS AND METHODS

Materials. Methyl glucoside, methyl galactoside (α types), β-octyl glucoside, stachyose and methyl oleate were purchased from Sigma Chemical Co. (St. Louis, MO). Sulfuric acid-dichromate solution (50%) H_2SO_4) was purchased from Supelco, Inc. (Bellefonte, PA). Naphthoresorcinol (1,3-naphthalenediol) was purchased from EM Science (Cherry Hill, NJ) and chromium acetyl acetonate was purchased from Aldrich Chemical Co. (Milwaukee, WI).

Acetylation of alkyl glycosides and stachyose. Acetylation of methyl glucoside, methyl galactoside, octyl glucoside and stachyose followed the procedures of Linstead *et al.* (5), except that an oil bath was used to supply heat instead of steam bath. The saccharide acetates were freeze dried, stored anhydrous over a desiccant and refrigerated until use.

Synthesis procedure and purification. Synthesis and purification of alkyl glycoside polyesters and stachyose polyesters followed the one-stage solvent-free synthesis procedures of Akoh and Swanson (2), with the exception that alkyl glycosde tetraacetates, stachyose tetradecaacetates (STAC) and fatty acid methly esters were reactants. The reaction parameters were varied to determine optimum conditions for synthesis using sodium metal as a catalyst to promote acyl migrations. Preliminary studies indicated that a mole ratio of alkyl glycoside tetraacetate:FAME 1:5 and STAC:FAME 1:14 gave optimum yields of the polyesters. Temperatures of 98-110°C, synthesis times of 2.5 hr, pressures of 0-5 mm

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Hg and catalyst concentrations of 1.5-2.0% Na metal (w/w) reactants were studied.

Methyl glucoside polyoleate. In a typical synthesis of methyl glucoside polyoleate, methyl oleate (113.94 g, 0.3843 mole) was poured into a three-necked, round-bottom flask and reaction apparatus described by Akoh and Swanson (2), and admixed with methyl glucoside tetraacetate (30 g, 0.0769 mole). Interesterification was carried out under a nitrogen atmosphere at temperatures of 98-105°C for 2.5 hr in the presence of sodium metal, 2% of the reactants w/w, 2.9 g. The mole ratio of methyl glucoside tetraacetate:methyl oleate was 1:5.

Substituting methyl glucoside tetraacetate with 30 g methyl galactoside tetraacetate and methyl oleate with 179.50 g peanut oil FAME yielded methyl galactoside polyesters of peanut oil. The peanut oil FAME were prepared according to the procedure of Akoh and Swanson (12).

Octyl glucoside polyester. Peanut oil FAME (143.50 g, 0.4900 mole) were mixed with octyl glucoside tetraacetate (50 g, 0.1077 mole) and 1.5% Na metal (2.90 g), and interesterification was carried out at 110°C for 2.5 hr (as previously described) to yield octyl glucoside polyester of peanut oil.

Stachyose polyoleate. In a typical synthesis of stachyose polyoleate, methyl oleate (95.35 g, 0.3216 mole), STAC (30 g, 0.0229 mole) and 2% Na metal (2.51 g) were admixed prior to the application of heat. Interesterification was carried out at 105-110°C for 2.5 hr. The mole ratio of STAC:methyl oleate was 1:14.

Infrared (IR) analyses. Infrared analyses of the purified liquid alkyl glycosides and stachyose polyesters were performed according to the conditions described by Akoh and Swanson (2).

Quantitative C-13 NMR analyses. The C-13 nuclear magnetic resonance spectroscopic analyses of the alkyl glycoside and stachyose acetates and purified alkyl glycosides and stachyose fatty acid polyesters were obtained with an NT-200 WB pulsed fourier-transform (FT) NMR spectrometer (Nicolet Magnetics Co., now GE NMR Instruments, Fremont, CA), equipped with a 12 mm probe operating at 50.3 MHz for C-13, a 45° or 90° pulse angles, and 2.5 sec or 10 sec repetition rates and broad band proton decoupling. Each 2.0000 g sample was dissolved in 5 ml deuterated chloroform ($CDCl_3$) containing 1% tetramethylsilane (TMS) and 0.03-0.04 N chromium acetyl acetonate (NMR relaxation reagent for quantitative NMR analysis), $Cr(AcAc)_3$. The spectra were obtained with no more than 32768 transients. Chemical shift data are reported relative to an internal standard TMS in parts per million (ppm). The deuterium signal of $CDCl_3$ was used as a field-frequency lock signal. Degree of substitution (D.S.) in the saccharide acetates and polyesters were determined by integrating the anomeric carbon peaks, acetate peaks, bound long chain fatty acid terminal methyl group and the average intensities of acetate and terminal methyl group peaks compared to the average peak area of the anomeric carbons used as a base.

Thin layer chromatography (TLC). TLC analyses of alkyl glycoside polyesters were performed using solvent systems I and II described by Akoh and Swanson (2), except TLC plates were sprayed with sulfuric acid dichromate solution. Glycoside polyesters were visualized as purple-violet spots on TLC plates when heated at 105°C for 5-10 min. The series of solvent systems used as mobile phase for stachyose polyester development were: System I—hexane:ethyl acetate 80:20, v/v (4); System II—petroleum ether:diethyl ether:acetic acid 75:25:1, v/v (13). Stachyose polyesters were detected by spraying developed plates with naphthoresorcinol reagent and observing purple-violet spots on a white background when heated at 105°C for 5-10 min.

Physical properties. Refractive indices (R.I.), specific gravity (sp. gr.), hydophile-lipophile balance (HLB) and apparent viscosity determinations were previously described (2,3).

RESULTS AND DISCUSSION

Table 1 presents reaction conditions and yields of alkyl glycoside and stachyose fatty acid polyesters synthesized by a one-stage solvent-free interesterification. A mole ratio of alkyl glycoside acetate:FAME 1:5 gave excellent yields of the pale yellow liquid alkyl glycoside polyesters. Acceptable yields of octyl glucoside polyesters of peanut oil, 98.8% yield was obtained with a sodium metal catalyst concentration of 1.5%. Optimum yields of stachyose polyoleate were obtained with a mole ratio of STAC: methyl oleate of 1:14. Temperatures between 98-110°C were required for optimum interesterification of saccharide acetates with long chain fatty acid methyl esters of both homogenous and heterogenous fatty acid composition. Low temperature, low pressure, short time reaction conditions have been reported for the synthesis of raffinose polyesters (2). According to Akoh and Swanson (2), sugar acetates exhibit melting points less than comparable sugars containing free hydroxyl groups. Acetates are good leaving groups, and protect sugars against degradation and caramelization during sugar polyesters synthesis. Alkyl glycoside tetraacetates used in the synthesis have melting points as previously determined by Differential Scanning Calorimetry (DSC):methyl glucoside tetraacetate, m.p. = 101.9°C; methyl galactoside tetraacetate, m.p. = 84.4°C; and stachyose tetradecaacetate (STAC), m.p. = 102.2°C. Addition of low melting acetates instead of glycosides with free OH groups, such

TABLE 1

Reaction Conditions and Yields of Alkyl Glycoside and Stachyose Polyesters

Type	Acetate:FAME[a]	Temperature (°C)	Yield (% by wt)
Methyl glucoside polyoleate	1:5	98-105	99.5
Methyl galactoside polyester of peanut oil	1:5	105-110	99.3
Octyl glucoside polyester of peanut oil	1:5	105-110	98.8
Stachyose polyoleate	1:14	105-110	99.2

[a] Acetate:FAME—Mole ratio of alkyl glycoside tetraacetate of STAC:FAME of peanut oil or methyl oleate.

as methyl glucoside, m.p. = 169–171°C (Aldrich Chemical Co., Milwaukee, WI), made interesterification at temperatures as low as 105°C possible.

Physical properties. The consistency of synthesized alkyl glycoside polyesters and stachyose polyesters closely resemble the consistency of conventional edible oils. The alkyl glycoside polyesters were pale yellow oils, while stachyose polyoleate was a golden yellow oil at room temperature (ca. 22°C). Table 2 presents the physical properties of alkyl glycoside and stachyose polyesters. The Refractive Index (R.I.), density and specific gravity of the polyesters approximated the R.I., density and sp. gr. of triolein and sucrose polyoleate, and were comparable to the R.I., density and sp. gr. of raffinose polyesters (2) and sucrose polyesters (3,14). Stachyose polyoleate, however, had slightly greater density and sp. gr. than the alkyl glycoside polyesters, but compared favorably with the density and sp. gr. of raffinose polyesters of soybean oil (2).

The hydrophile-lipophile balance (HLB) values of alkyl glycoside and stachyose polyesters are presented in Table 2. The HLB values for methyl glucoside, methyl galactoside and octyl glucoside polyesters were similar to the HLB value of sucrose polyoleate (HLB 3.5). However, stachyose polyoleate has a slightly greater HLB value (5.0) than the glycoside polyesters, but similar to the HLB value of 6.0 reported for raffinose polyoleate (3). HLB values are indicators of behavioral characteristics and do not indicate emulsifying efficiency. HLB values of the polyesters were obtained relative to emulsifying properties of surfactants with known HLB values (3).

The HLB values of alkyl glycoside and stachyose polyesters were between three and five, suggesting a lipophilic nature and potential for application in water-in-oil emulsions such as margarine and butter. Both alkyl glycoside polyesters and stachyose polyoleate were insoluble in water at 25°C and 75°C, but soluble in vegetable oil, hexane and chloroform at 25°C and 75°C, suggesting the polyesters are nonpolar molecules.

The apparent viscosities of methyl glucoside polyoleate, and methyl galactoside and octyl glucoside polyesters of peanut oil approximated the apparent viscosity of triolein. The apparent viscosities of stachyose polyoleate were similar to the apparent viscosities of sucrose polyoleate and sucrose polyester of soybean oil (3). Hamm (11) reported that SPE with a degree of substitution ranging from four to eight exhibited apparent viscosities in the range of vegetable oils. Jandacek and Webb (14) reported apparent viscosities greater than apparent viscosities reported by Hamm (11) for completely esterified SPE. Apparent viscosities reported for alkyl glycoside polyesters were similar to apparent viscosities of triolein, suggesting that polar methoxy (OCH_3) and relatively polar octyl groups may contribute to reduced apparent viscosities for glycoside polyesters relative to nonpolar sucrose polyesters.

Preliminary lipase challenge studies indicated that stachyose polyester and alkyl glycoside polyesters were not susceptible to *in vitro* lipolysis, suggesting potential application as low calorie oil substitutes. *In vivo* methyl glucoside polyester feeding trials with mice (15) indicated that alkyl glycoside polyesters could be used for weight reduction.

Product structure confirmation. Figure 1 presents the IR spectra of methyl glucoside polyoleate. Absorption bands were observed at 3480 cm^{-1} (overtone stretching vibrations of C=O), 3000–2850 cm^{-1} (C–H stretch in CH_3 and/or CH_2), 1740 cm^{-1} (ester C=O), 1460 cm^{-1} (C–H stretch in CH_3 and/or CH_2) and 920 cm^{-1} (pyranose ring). The IR spectra of stachyose polyoleate (Fig. 2) contained absorption bands at 3480 cm^{-1} (weak overtone bands of C=O stretch) and 3000–2850 cm^{-1} (C–H stretch in CH_3 and/or CH_2). Table 3 illustrates the characteristic IR absorption bands of methyl galactoside and octyl glucoside polyesters of peanut oil. The two spectra are similar except that the pyranose ring in the methyl galactoside polyester absorbed at 910 cm^{-1}, and the

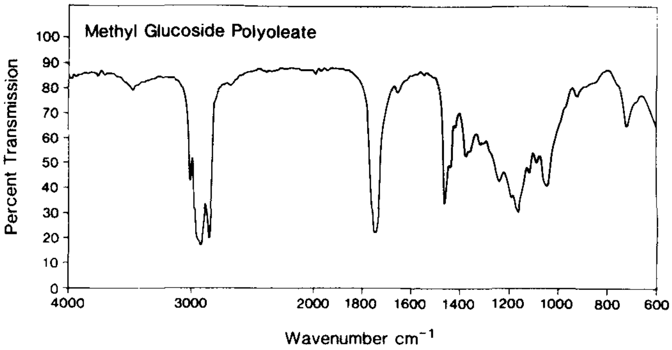

FIG. 1. IR spectrum of methyl glucoside polyoleate.

TABLE 2

Properties of Alkyl Glycoside and Stachyose Polyesters

Type	HLB	R.I. (at 40°C)	Density g/cm^3 (at 20/20°C)	Sp. gr. (at 20/20°C)	Viscosity at 20°C (cp)
Methyl glucoside polyoleate	3.4	1.4668	0.9139	0.9155	135
Methyl galactoside polyester of peanut oil	3.4	1.4672	0.9229	0.9245	138
Octyl glucoside polyester of peanut oil	3.2	1.4670	0.8995	0.9011	140
Stachyose polyoleate	5.0	1.4673	0.9451	0.9468	240
Triolein	—	1.4626	0.9131	0.9148	150
Sucrose polyoleate	3.5	1.4688	0.9152	0.9136	235

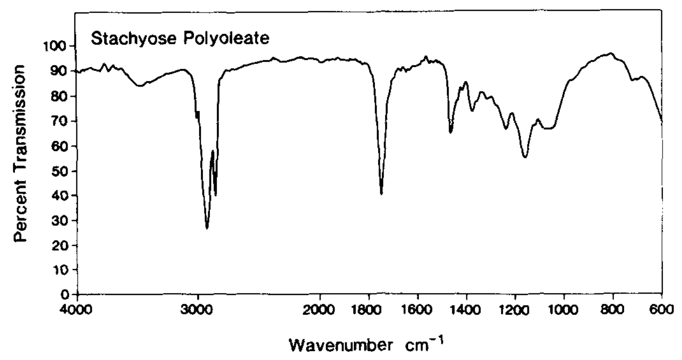

FIG. 2. IR spectrum of stachyose polyoleate.

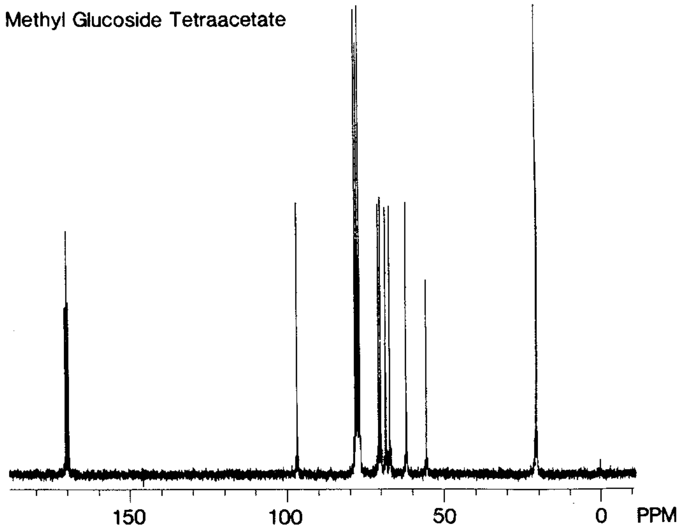

FIG. 3. C-13 NMR spectrum of methyl glucoside tetraacetate in $CDCl_3$-TMS.

TABLE 3

Infrared Spectroscopic Data for Methyl Galactoside and Octyl Glucoside Polyesters of Peanut Oil

Type	Absorption (cm^{-1})	Assignment
Methyl galactoside polyester	3480	C=O overtones
	3000-2845	C-H stretch in CH_3 and/or CH_2
	1750	ester C=O
	1460	C-H def. in CH_3 and/or CH_2
	1370	C-H def. in CH_3
	910	pyranose ring
Octyl glucoside polyester	3480	C=O overtones
	3020-2860	C-H str. in CH_3 and/or CH_2
	1750	ester C=O
	1460	C-H def. in CH_3 and/or CH_2
	1380	C-H def. in CH_3
	940	β linkage
	915	pyranose ring

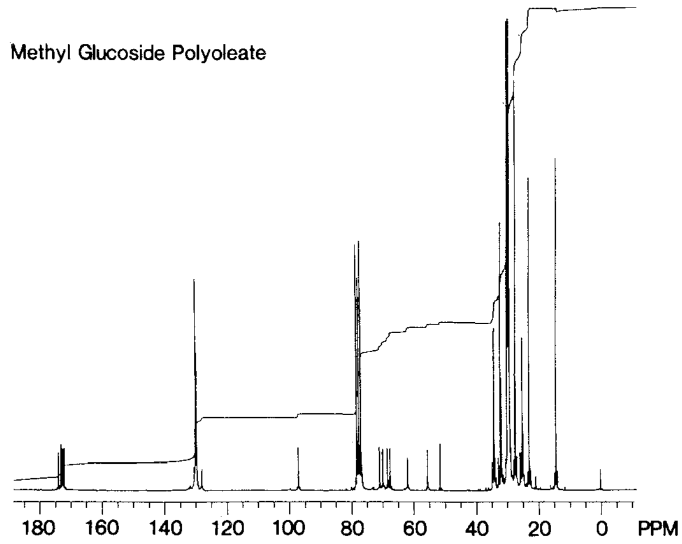

FIG. 4. C-13 NMR spectrum of methyl glucoside polyoleate in $CDCl_3$-TMS.

pyranose ring in octyl glucoside absorbed at 915 cm^{-1}. The β linkage in octyl glucoside was tentatively identified with absorption at 940 cm^{-1}.

Figure 3 is a C-13 NMR spectrum of methyl glucoside tetraacetate in $CDCl_3$-TMS containing 0.04 N chromium acetyl acetonate. In the spectrum, signals representing acetyl methyl carbons (20.2 ppm), methoxy group (54.9 ppm), the C_6 of glucose (61.4 ppm), other carbons of the glucose skeleton (66.6-70.2 ppm), $CDCl_3$ (76.3-77.6 ppm), the anomeric carbon of glucose (96.2 ppm) and carbonyl carbons of the acetyl group (168.9-170.0 ppm) were observed. In the C-13 NMR spectrum of methyl glucoside polyoleate (Fig. 4) signals observed include the end methyl carbons of oleic acid (14.1 ppm), the CH_2 group of oleic acid (22.7-34.0 ppm), the methoxy group (55.3 ppm), the C_6 of glucose (61.7 ppm), other carbons of glucose (67.4-70.4 ppm), $CDCl_3$ (76.7-78.0 ppm), the anomeric carbon of glucose (96.8 ppm), C18:1 (127.8-129.8 ppm) and the carbonyl carbons of oleoyl group (172.0-173.9 ppm).

Figure 5 is the C-13 NMR spectrum of stachyose polyoleate in $CDCl_3$-TMS containing 0.04 N $Cr(AcAc)_3$ assayed at a 2.5 sec repetition rate and 90° pulse angle. In the spectrum, signals of the end methyl carbons of oleic acid (14.1 ppm), residual acetate (20.7 ppm), CH_2 of oleic acid (22.7-34.7 ppm), carbon skeletons of stachyose (61.6-70.1 ppm), $CDCl_3$ (76.3-78.0 ppm), anomeric carbons (90.4, 96.3 and 104.6 ppm), C18:1 (127.9-130.1 ppm) and carbonyl carbons of oleoyl group (171.9-174.1 ppm) were observed.

Figure 6 is the C-13 NMR spectrum of methyl galactoside tetraacetate in $CDCl_3$-TMS containing 0.04 N chromium acetyl acetonate assayed at a 2.5 sec repetition rate and 45° pulse angle. Signals observed include the acetyl methyl carbons (20.6-20.7 ppm), methoxy group (55.4 ppm), C_6 of galactose (61.7 ppm), carbon

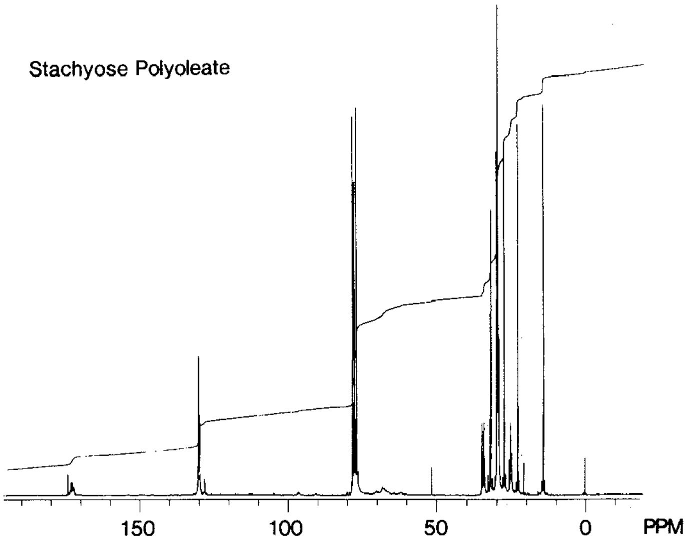

FIG. 5. C-13 NMR spectrum of stachyose polyoleate in $CDCl_3$-TMS, 90° pulse angle.

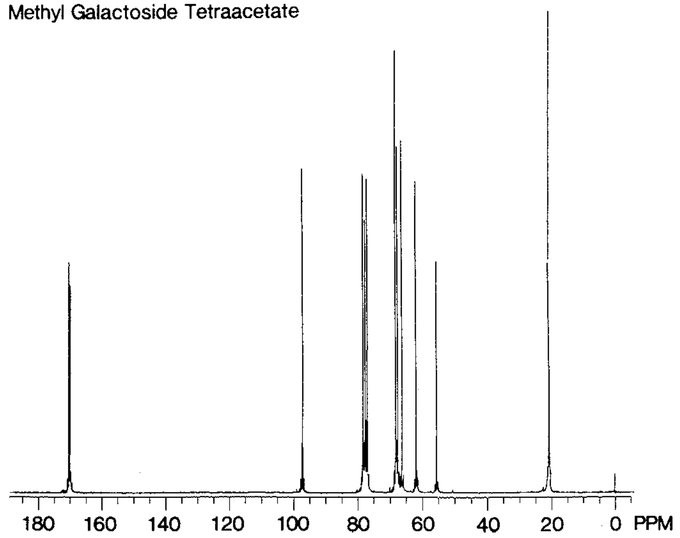

FIG. 6. C-13 NMR spectrum of methyl galactoside tetraacetate in $CDCl_3$-TMS, 45° pulse angle.

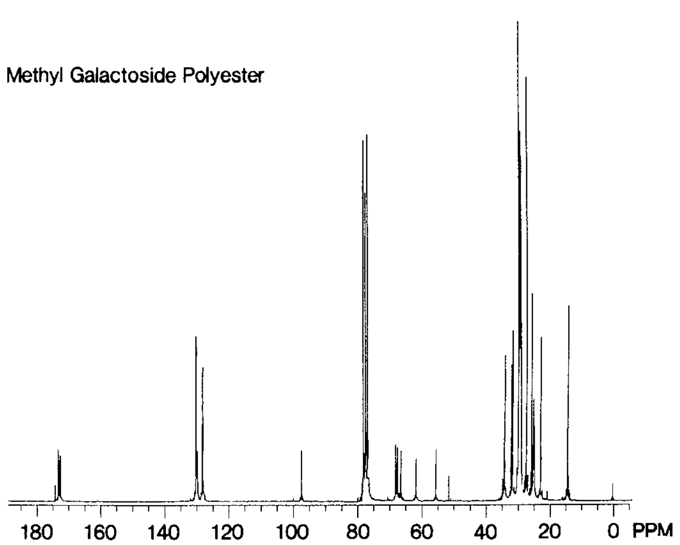

FIG. 7. C-13 NMR spectrum of methyl galactoside polyester of peanut oil in $CDCl_3$-TMS.

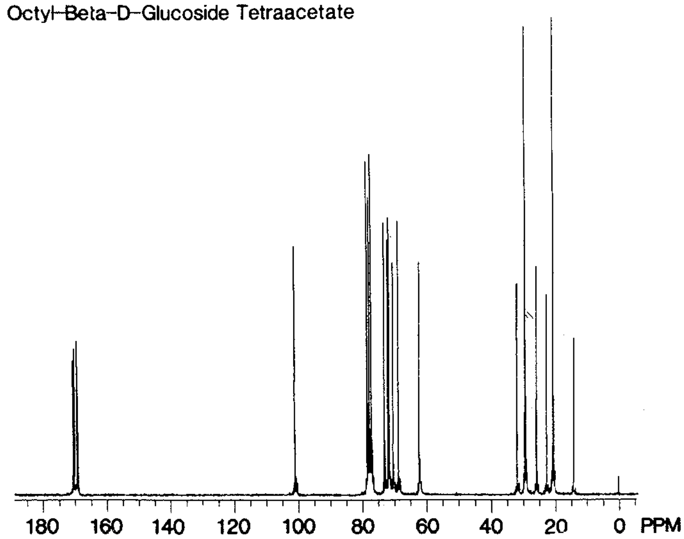

FIG. 8. C-13 NMR spectrum of octyl glucoside tetraacetate in $CDCl_3$-TMS containing 0.04 N Cr(Ac Ac)$_3$.

skeleton of galactose (66.1–68.0 ppm), $CDCl_3$ (76.0–79.1 ppm), anomeric carbon of galactose (97.1 ppm) and carbonyl carbons of acetyl group (169.2–170.6 ppm). In the spectrum of methyl galactoside polyester of peanut oil methyl galactoside polyester of peanut oil (Fig. 7) signals observed include the end methyl carbons of the long chain fatty acids (14.1 ppm), residual acetate (20.7 ppm), methylene group of peanut oil fatty acids (22.7–34.0 ppm), methoxy group (55.4 ppm), C_6 of galactose (61.6 ppm), carbon skeleton of galactose (66.3–67.9 ppm), $CDCl_3$ (76.2–78.4 ppm), anomeric carbon of galactose (97.3 ppm), C18:1 and C18:2 (127.6–130.3 ppm) and carbonyl carbons of acyl group (172.3–174.0 ppm).

Figure 8 is the C-13 NMR spectrum of octyl glucoside tetraacetate in $CDCl_3$-TMS containing 0.04 N Cr(AcAc)$_3$. In the spectrum, signals for end methyl carbons of octyl group (14.0 ppm, diagnostic for octyl group), C_6 of glucose (61.9 ppm), carbon skeleton of glucose and CH_2 attached to oxygen in octyl group, OCH_2 (68.4–72.8 ppm), $CDCl_3$ (76.4–78.6 ppm), anomeric carbon of glucose (100.7 ppm) and carbonyl carbons of octyl group (169.0–170.4 ppm) were observed. Figure 9 is the C-13 NMR spectrum of octyl glucoside polyester of peanut oil obtained under the same conditions as octyl glucoside acetate. Signals observed include the end methyl carbons of both octyl and long chain fatty acids of peanut oil (14.1 ppm), CH_2 of octyl and peanut oil fatty acids (22.7–34.0 ppm), C_6 of glucose (61.8 ppm), carbon skeleton of glucose and CH_2 attached to oxygen in octyl group, OCH_2 (68.2–72.5 ppm), $CDCl_3$ (76.2–78.4 ppm), anomeric carbon of glucose (100.8 ppm), C18:1 and C18:2 (127.8–130.5 ppm) and carbonyl carbons of acyl group (171.8–174.0 ppm).

The IR spectral data confirmed the structures of the alkyl glycoside polyesters and stachyose polyester,

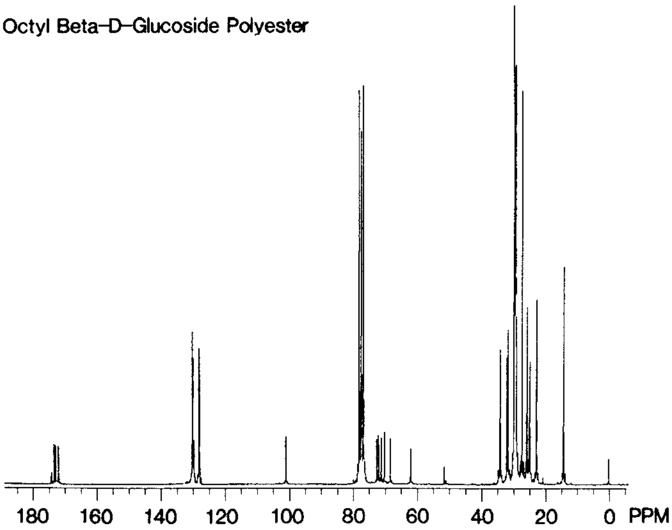

FIG. 9. C-13 NMR spectrum of octyl glucoside polyester of peanut oil in $CDCl_3$-TMS containing 0.04 N $Cr(Ac\ Ac)_3$.

TABLE 4

Degree of Substitution in Alkyl Glycoside and Stachyose Polyesters by C-13 NMR Spectroscopy

	Integral		
Type	Anomeric carbons (base)	Terminal CH_3 of bound long chain fatty acids	Calculated D.S. ± 0.10
Methyl glucoside polyoleate	100	448.04	4.48
Methyl galactoside polyester of peanut oil	1000	3357.56	3.36
Octyl glucoside polyester of peanut oil	1000	4211.07	4.21
Stachyose polyoleate	100	1239.64	12.40

respectively. Further evidence of successful synthesis was obtained from TLC data. For example, methyl glucoside tetraacetate had an $R_f = 0.10$; methyl oleate, $R_f = 0.77$; sucrose polyoleate, $R_f = 0.90$; methyl glucoside polyoleate, $R_f = 0.83$ on a TLC plate developed with the solvent system consisting of petroleum ether:ether:acetic acid 75:25:1, v/v (13). Methyl glucoside remained at the origin. The TLC plates were sprayed with sulfuric-acid dichromate (50% H_2SO_4) and alkyl glycoside polyesters appeared as purple-violet spots. The TLC plate was sprayed with naphthoresorcinol reagent after development to give a purple-violet spot of stachyose polyoleate on a white background.

Degree of substitution (D.S.). Table 4 illustrates the use of C-13 NMR spectroscopic data as an analytical tool in the determining of the degree of substitution in alkyl glycoside and stachyose polyesters. The approximate degree of substitution in purified polyesters were calculated by taking the integral of the anomeric carbon peaks: 96.8 ppm for methyl glucoside polyoleate; 90.4, 96.3 and 104.6 ppm for stachyose polyoleate; 97.3 ppm for methyl galactoside polyester and 100.7 ppm for octyl glucoside polyester. The mean peak area of each glycoside or stachyose anomeric carbon was used as a base for comparison. The peak areas of residual acetate peaks at about 20.2–20.7 ppm, were also integrated. The integrated mean peak area of the anomeric carbons were compared to integrated peak areas of the bound long chain fatty acids, 14.1 ppm, terminal methyl group, the mean intensity of OCH_3 and octyl groups, respectively. From Table 4, the calculated D.S. for methyl glucoside polyoleate was 4.48, methyl galactoside polyester of peanut oil 3.36, octyl glucoside polyester of peanut oil 4.21 and stachyose polyoleate 12.40, indicating a high degree of substitution of the acetate groups with long chain fatty acids. The degree of substitution were reproducible to within ± 0.10 units. As an illustration, comparison of the ratio of anomeric carbon to the methyl, methoxy or acetate groups gave the following results: (a) methyl glucoside polyoleate—anomeric vs CH_3 = 1:4.48, anomeric vs OCH_3 = 1:1, anomeric vs acetate = 1:0.1; (b) methyl galactoside polyester of peanut oil—anomeric vs CH_3 = 1:3.4, anomeric vs OCH_3 = 1:0.9, anomeric vs acetate = 1:0.2.

The anomeric carbon ratios indicated that loss of methoxy or octyl groups during the interesterification process was unlikely. The retention of the methoxy or octyl groups was confirmed from the C-13 NMR spectra data (Figs. 4, 7 and 9) and the ratio of anomeric carbons and methoxy groups.

The use of C-13 NMR as an analytical tool in quantifying D.S. in carbohydrate polyesters was suggested by Akoh and Swanson (2). Pfeffer *et al.* (16) reported the use of analytical C-13 NMR as a rapid, nondestructive tool for determining the *cis, trans* composition of catalytically treated unsaturated lipid mixtures. Paramagnetic relaxation reagents such as chromium acetyl acetonate [$Cr(AcAc)_3$] can be used to obtain quantitative C-13 NMR data (17). Dissolving a paramagnetic additive introduces a powerful relaxation mechanism which shortens the T_1s of all carbons so that relaxation time differentials become insignificant. However, deviation from this behavior may be encountered for carbons which are buried at the interior of the polyester molecule. The use of C-13 NMR to quantitate D.S. in carbohydrate polyesters synthesized from their acetates as starting materials appears to be promising for quantification of carbohydrate fatty acid polyesters. However, if the size of the carbohydrate increases and the degree of substitution of the acetate groups with long chain fatty acids increases, then the carbohydrate polyester produced become so large that signals from the sugar backbone carbons in C-13 NMR spectrum become small. Akoh and Swanson (2) observed that the high degree of substitution in raffinose polyester molecule made signals from the sugar backbone carbons small. To quantitate D.S. in stachyose or raffinose fatty acids polyesters, the sugar backbone carbons must be expanded.

Alkyl glycoside fatty acid polyesters and stachyose fatty acid polyester can be synthesized by a one-stage solvent-free interesterification process. The use of alkyl glycoside polyesters as low calorie fat substitutes may offer an economical alternative to sucrose polyesters because glucose is an inexpensive, readily available material. The physical properties of alkyl glycosides and stachyose polyesters were not markedly different from the physical properties of sucrose polyesters (SPE) or conventional triglycerides. C-13 NMR was useful in quantitating the degree of substitution in the purified alkyl glycosides and stachyose polyesters.

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