Syntheses and Characterizations of Insecticidal Sucrose Esters

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New types of sucrose esters have been synthesized and shown to be potent insecticides against sweet potato whiteflies. On the basis of the structures of natural sucrose esters isolated from various *Nicotiana* species and which were shown to be potent whitefly insecticides, it was decided to synthesize similar sucrose esters. Specific conditions were worked out for the reaction of acid chloride with sucrose to yield a series of mono-, di-, tri-, and tetraacyl sucroses. As the active sucrose esters of *Nicotiana* species contain mainly heptanoic and octanoic acids esterified to sucrose, C_6-C_{12} aliphatic acid sucrose esters were prepared. Capillary gas chromatography of their TMS derivatives showed that distinct groups of isomers were produced. Separation by silicic acid chromatography produced fractions containing individual groups of monoacyl sucroses, diacyl sucroses, triacyl sucroses, etc. Evaluations of individual groups of the C_6-C_{12} acid sucroses showed that diheptanoyl sucroses, dioctanoyl sucroses, and dinonanoyl sucroses were most active against whiteflies and aphids. Details of syntheses, separations, GC and NMR data, and whitefly assays are presented.

Keywords: *Sugar esters; insecticides; whiteflies; aphids; chromatography; syntheses; bioassays; correlation*

INTRODUCTION

As sugars have a number of free alcoholic hydroxyl groups, their reactions with aliphatic or aromatic acids produce sugar esters having one or more acyl groups in the sugar ester molecule. Sugar esters have been found to occur naturally in plants and are being commercially produced for the food industry.

Extensive research in the early 1960s led to the production of large quantities of stearic and palmitic sucrose esters for use as emulsifiers in cakes, biscuits, chocolates, candy, ice cream, etc., and as stabilizers and wetting agents, while lauric and oleic acid sugar esters were produced for use as detergent surfactants (Kosaka and Yamada, 1977). The food applications of sucrose esters (Walker, 1984) have been extended to their use as solubilizers for poorly water soluble drugs (Hahn and Sucker, 1989). As more than one fatty acid could be added to sucrose, the preparations of sucrose esters ranged from monoesters to sucrose polyesters. In recent years, work on sucrose polyesters has concentrated on their use as low-calorie fat (Olestra) and oil substitutes (Akoh and Swanson, 1990) leading to a world market of about $75 million for these additives or substitutes (Elsner et al., 1991).

On the other hand, sucrose esters obtained from plants have yet to be developed to such an extent. Plant sucrose or glucose esters are composed of the lower fatty acids (C_2-C_{10}) and possess very interesting biological properties. Sucrose esters have been found in wild tomato and wild potato species (King et al., 1988, 1993 and references therein) and have been related to aphid resistance (Neal et al., 1990) and antifungal properties (Holley et al., 1987). Exudates from the trichomes of tomato leaves have revealed the presence of glucose esters in the polar lipids (Burke et al., 1987; Goffreda et al., 1990). More recently, our work has shown the presence of glucose and sucrose esters in petunias (Kays et al., 1994), and their structures will be reported shortly.

Perhaps, the most interesting plants are those of the *Nicotiana* family, whose species, including *Nicotiana tabacum*, the commercial tobacco plant, have been the source of a large and diverse group of both glucose and sucrose esters. One of our laboratory's works characterized the levels and compositions of both glucose and sucrose esters of 50 *Nicotiana* species (Severson et al., 1991). Acids esterified to sucrose or glucose were generally methyl-branched and ranged from C_2 to C_8 aliphatic acids, with methyl groups on the 2, 3, or 4 carbon of the acids. The most predominant sucrose esters had acyl groups on the hydroxyl groups of the 2, 3, and 4 carbons of the glucose portion. Such structures have been deduced from ^{13}C-NMR and mass spectrometry data (Arrendale et al., 1990; Matsuzaki et al., 1991). One of the most interesting species that has been extensively examined is *Nicotiana gossei* (Severson et al., 1994), mainly due to the fact that its sucrose esters have shown potent toxicity against the greenhouse whitefly (Buta et al., 1993). The subsequent patent (Pittarelli et al., 1993) on the whitefly toxicities of sugar esters of the *Nicotiana* species indicated that the activity was due to 2,3-di-*O*-acyl-1′,6′-di-*O*-acetylsucroses, with the acyl groups being mainly 5-methylhexanoyl and 5-methylheptanoyl groups. Such potent insecticidal activities of natural sucrose esters against the persistent

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and damaging whiteflies (over $200 million losses annually in the United States alone) have shown that sugar esters are a new class of "natural" insecticides that should be exploited for commercial use.

As the sugars are produced in the glandular secretions of leaf hairs (trichomes) of the *Nicotiana* plants, their levels on *Nicotiana* species leaf surfaces are very small, being generally less than 100 $\mu g/cm^2$ of leaf surface (Severson et al., 1991). Our recent studies (to be published) on yields of sugar esters from large scale field productions showed that the best producer of active sucrose esters was *Nicotiana trigonophylla*, yielding sugar esters at 158 $\mu g/cm^2$ (2.8 g/kg of plant material). Therefore, plants cannot serve as sources of commercial quantities of the insecticidal sucrose esters. As more and more studies are showing the potency of naturally-occurring sugar esters as pesticides, the need exists to identify and synthesize specific synthetic sugar ester pesticides for use against whiteflies and other soft-bodied arthropod pests, which are damaging our agricultural products.

MATERIALS AND METHODS

Sucrose Esters (SE) Synthesis. To maximize the formation of diacyl sucrose esters, 1 mol of sucrose was reacted with 2.25 mol of acid chloride. Thus, for example, sucrose was dissolved in dimethylformamide at a concentration of 54.8 g (0.16 mol) of sucrose/100 mL of DMF (in a 1 L Erlenmeyer flask), with gentle heating (up to 100 °C) and stirring on a magnetic stirrer/hot plate, until the sucrose dissolved. Then, 40 mL of pyridine was added, and the solution was cooled to 65 °C. The flask was returned to a magnetic stirrer plate, a thermometer was inserted into the flask, and the solution was stirred vigorously as the acid chloride solution was added. Acid chloride (0.36 mol) was dissolved in 150 mL of acetonitrile and poured into a separatory funnel, and this solution was added at a fast drop rate (over a 45 min period) to the sucrose solution, while stirring vigorously. (Acid chlorides ranged from hexanoyl to dodecanoyl chloride.) Acid chlorides must be added as a CH_3CN solution, otherwise extensive degradation of SE to glucose esters will occur. The reaction temperature was maintained at 65 °C, with cooling of the flask in a water bath, if needed. After addition of the acid chloride, the reaction mixture was stirred for 1 h at 65 °C, cooled to about 40 °C, and poured into 200 mL of acetone. About 34 g of sodium bicarbonate (0.4 mol) was mixed with 5 mL of water, and the paste was added slowly into the reaction mixture to decompose the pyridine hydrochloride product. After the evolution of CO_2 ceased, anhydrous, crystalline sodium sulfate (200 g) was added. At this point, the reaction mixture liquid was clear and pale yellow. The reaction mixture was then filtered and evaporated to dryness on a rotary evaporator, with the water bath temperature below 40 °C. A vacuum pump was required to remove any residual solvents (such as dimethylformamide). The yield of total SE was generally 85–90%, in addition to about 5% glucose esters, 5% unreacted sucrose, and smaller amounts of α- and β-D-glucose. The SE mixture was generally composed of 20–30% monoacyl sucroses, 35–45% diacyl sucroses, 14–25% triacyl sucroses, and 5–10% tetraacyl sucroses, as determined by GC.

Chromatographic Separation of Sucrose Esters on Silicic Acid (SA). The reaction products, dissolved in chloroform, were separated on activated SA using a solvent system of increasing percentages of methanol in methylene chloride. About 300 g of 100–200 mesh silicic acid (Unisil SA from Clarkson Chemical Co. or 100 mesh silicic acid from Sigma Chemical Co.) was required to separate 15–20 g of reaction product. The silicic acid, slurried in methylene chloride, was packed into a glass column (90 × 4 cm) equipped with a 500 mL reservoir and a ball joint at the top of the reservoir to allow the use of air or nitrogen pressure and clamps. The reaction product (15 g in 60 mL of $CHCl_3$) was added to the top of the SA column. Air pressure, at 2 psi, was used to push the solvents rapidly through the column. The column was eluted with 500 mL volumes of the following percentages of methanol in methylene chloride: 0%, 1%, 2%, 2.5%, 3%, 3.5%, 4%, 4%, 5%, 5%, 5.5%,6%, 6%, 6.5%, 7%, 7%, 7.5%, 8%, 10%, 12%, 14%, and 16%. (The small increases in the percentages of methanol were required to separate the individual groups of sucrose esters.) The resulting chromatographic fractions were concentrated to dryness on a rotary evaporator (40 °C) in round bottom flasks. Methanol (5 mL) was added to each fraction to redissolve the residue, and 2–3 μL was removed for gas chromatographic analysis.

Spinning thin-layer chromatography was performed on a chromatotron, model B #7924T (Harrison Research Inc., 840 Moana Ct., Palo Alto, CA). A circular (9.5 in.) glass plate (rotor) was coated with a 2 mm layer of silica gel 60 (EM Science). The SE sample was applied as a methylene chloride solution, and the plate was dried. The eluting solvent system was a gradient of 0–10% methanol in methylene chloride, pumped at a rate of 3 mL/min. Fractions (10 mL) were collected.

Gas Chromatography (GC). The sucrose esters obtained in the SA fractions as well as in the original reaction products were characterized by GC of their trimethylsilyl (TMS) ether derivatives. To form the volatile GC derivatives, sugar esters were derivatized by reacting them with *N,O*-bis(trimethylsilyl)-trifluoroacetamide (BSTFA) and dimethylformamide (DMF) in GC autosampler vials, which were sealed and heated at 75 °C for 1 h (Severson et al., 1984). One microliter samples were injected into a 0.32 mm × 30 m glass capillary GC column, coated with 0.1 μm of DB 5HT (J&W Scientific Co.). The GC oven was programmed from 80 to 390 °C at 5 °C/min, the injection port and detector of the instrument (Hewlett Packard 5890) were set to 350 °C, and the carrier gas (H_2) flow rate was set at 35 cm/s.

Mass Spectrometry. Total SE reaction products, as well as SA or other liquid chromatography fractions, were analyzed as their TMS derivatives with a Hewlett Packard 5989A GC–MS instrument. Total ion chromatograms were obtained. The GC–MS interface temperature was 280 °C, the ion source temperature was 250 °C, and the electron impact (EI) ionization energy was 70 eV for each analysis. Other MS conditions for the analyses were scan range of 40–650 Da, 0.88 scans/s, and electron multiplier voltage of 1866 volts. The GC column and conditions were the same as for the GC analyses.

Magnetic Resonance Spectrometry. All proton (^1H) and carbon (^{13}C) experiments were performed with a Brucker 400 MHz instrument (Aspect 3000) interfaced to a Brucker FDD 280 data system. Multiplicity, broad-band decoupling, COSY, HETCOR, and *J*-resolve experiments were done according to the Brucker operations manual and techniques described by Nakanishi (1990) and Derome (1990). The substituted sugars were in acetone-d_6 solutions contained in 5 mm tubes.

Whitefly Bioassay. SE products or individual SE groups (10.0 mg) were placed into 20 mL scintillation vials and dissolved in 500 μL of methanol. Water (9.5 mL) was added, and the vial was sonicated for 10 min. Methanol (5%)–water was used as control. Adult whiteflies (*Bemisia tabaci* Gennadius, B. strain) were knocked from sweet potato plants onto yellow Sticky strips (Olson Products Inc., Medina, OH) on damp paper towels in flat plastic boxes, in a bioassay first devised by G. W. Pittarelli (personal communication). Each strip was 3 cm × 14 cm with two 3 cm square areas of sticky surface exposed, onto which approximately 30 adults/square adhered. Two strips were used per treatment. Treatment applications were replicated on different dates. The strips were sprayed with test compound solutions (2 mL), using an airbrush (Badger 2000), with a fine-mist nozzle setting from a distance of 30 cm, in a laboratory fume hood. Counts for mortality were made 2 h after spraying using a binocular microscope.

Tobacco Aphid Bioassay. Aqueous dispersions of sugar ester fractions, obtained from the column chromatographic step, or the total reaction SE products, were sprayed on greenhouse-reared apterous (wingless) aphids. Sugar ester products or individual SE groups (10.0 mg) were placed into 20 mL scintillation vials and dissolved in 500 μL of acetone.

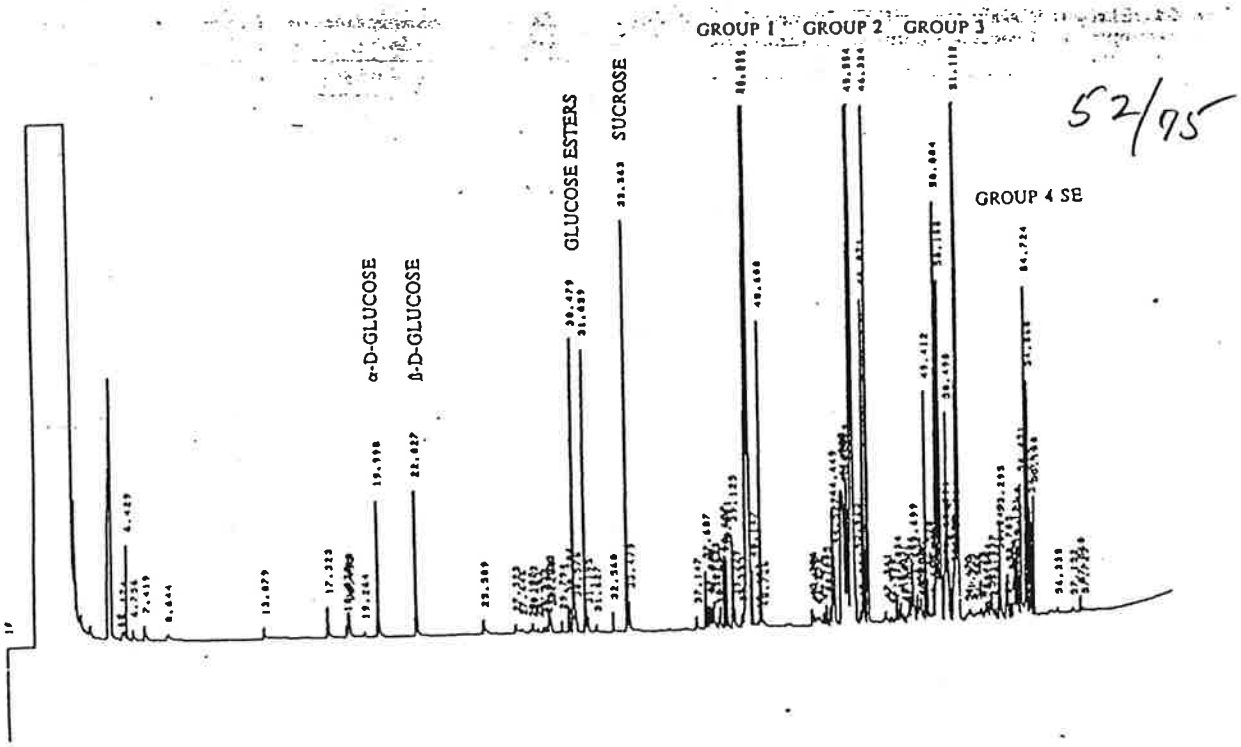

Figure 1. Gas chromatogram of total octanoyl sucrose ester reaction products (TMS derivatives).

Distilled water (9.5 mL) was added to each vial and sonicated for 10 min just prior to treatment applications. Acetone (5%)–water was used as a control. Small tobacco bud leaves (5–9 cm) infested with apterous tobacco aphid (Myzus *nicotiana* Blackman) nymphs were collected from greenhouse plants. Each leaf was considered one replication and sprayed with a designated sucrose ester at a rate of 1 mg/mL of water and placed in a petri dish (9 cm × 1.5 cm) fitted with moistened filter paper. Four replications were used for each treatment. Aphids were treated with an airbrush (Binks-B) using a fine-mist nozzle setting by spraying both sides of each leaf with the test solutions from a distance of 8 cm. Leaves were sprayed to run off with test compound solutions by passing the airbrush across each leaf surface four times while spraying. Percent mortality was determined after 24 h using a binocular microscope.

RESULTS AND DISCUSSION

The sucrose esters were prepared under specially developed conditions but according to the standard reaction of acid chlorides and alcohols to form esters. The synthetic conditions developed as follows. Generally, esterifications are conducted under anhydrous conditions by adding a solution of an acid chloride to a solution of the alcohol. Unfortunately, sugars, such as sucrose, cannot be dissolved in standard solvents such as chloroform, acetone, acetonitrile, or benzene, and polar solvents such as methanol or ethanol cannot be used as they would compete in the reaction to form methyl or ethyl esters of the acids. The literature revealed a large variety of methods for the formation of palmitic, stearic, or oleic esters of sucrose. Generally, these sucrose esters were prepared by transesterification of fatty acid methyl esters with sucrose with catalysts such as K_2CO_3, molten sodium, or lithium or potassium soaps at high temperatures (180 °C) and with or without solvents (Kurtz, 1966; Feuge et al., 1970; Akoh and Swanson, 1989; Osipow and Rosenblatt, 1967; Rizzi and Taylor, 1978). As these conditions appeared rather drastic and generally produced mostly monoesters, another approach was needed.

As most natural sucrose esters that exhibit insecticidal activities are di- and triacyl sucroses, where the acyl groups are heptanoic or octanoic acids, it was decided to modify the reaction as to prepare mostly di- and trioctanoyl sucroses. The most logical approach appeared to be the addition of 3 mol of acid chloride to 1 mol of sucrose in solution, with pyridine present to neutralize the HCl from the reaction. This seemed reasonable as a literature method (Youngs, 1958) described the formation of tristearin by heating 3 mol of steroyl chloride with glycerol at 100 °C and 2 mm pressure. The problem of a suitable solvent for sucrose was overcome by using dimethylformamide. Solutions of sucrose in DMF were readily prepared by slowly heating sucrose with DMF, with vigorous stirring, to 100 °C. Then the pyridine and octanoic acid chloride were added. Although, sugar esters were formed, they were mostly monooctanoyl sucroses. The final syntheses was developed after much trial and error. The best reaction conditions involved the slow addition of 2.25 mol of acid chloride in acetonitrile to a solution of 1 mol of sucrose in DMF and pyridine at 65 °C. (Higher molar ratios yielded more of the tri-, tetra-, and pentaacyl sucroses.) These conditions yielded mono-, di-, tri-, and tetraacyl sucroses, as shown by the gas chromatogram in Figure 1.

As sucrose has eight free hydroxyl groups, esterification with octanoic acid could result in the formation of eight groups of sucrose esters: monooctanoyl sucroses (called "group 1"), dioctanoyl sucroses (called "group 2"), trioctanoyl sucroses (called "group 3"), tetraoctanoyl sucroses (called "group 4"), etc., all the way up to octaoctanoyl sucrose. For monooctanoyl sucroses, octanoic acid can attach to any one of the eight hydroxyls of sucrose to give eight different positional isomers. Group 2 SE, which have two acids esterified to two hydroxyls, could also have a large number of isomers

Table 1. Percent Distribution of SE Groups in Chromatographic Fractions from an Octanoyl SE Preparation[a]

fraction (%) of CH_3OH in CH_2Cl_2	SE group 1	2	3	4	5
2			10	79	10
2.5			13	71	8
3			80	18	
3.5		7	93		
4		35	64		
4		87	24		
5		90	8		
5		87			
5.5		99			
6		95			
6		100			
6.5		100			
7		100			
7	6	94			
7.5	37	58			
8	80	20			
10	94	6			
12	99	1			
14	100				
16	100				

[a] Calculated from peak areas of GC data for each fraction.

(27), such as 2,3-, 2,4-, 2,6-, 3,4-, 3,6-, 4,6-, 1′,2-, 1′,3-, 1′,4′-, 1′,6-, etc., dioctanoyl sucrose. (Glucose carbons are numbered 1–6; fructose carbons are 1′–6′.) Similarly group 3 SE could have a large number of possible isomers. As seen from Figure 1, the reaction only produced a few of the possible isomers. There are only three major monooctanoyl sucrose compounds in group 1, one very predominant dioctanoyl sucrose with two lesser dioctanoyl sucroses in group 2, one major trioctanoyl sucrose and four minor trioctanoyl sucroses in group 3, and two major and several minor tetraoctanoyl sucrose esters in group 4. The acylation of sucrose has been studied and shown to be selective for certain hydroxy groups (Chowdhary et al., 1984), and therefore a much smaller number of isomers in each group is obtained.

In order to determine the structures of these sucrose compounds as well as their insecticidal activities, it was necessary to effect a major chromatographic separation. For this purpose, a total octanoyl sucrose ester reaction product was subjected to column chromatography on silicic acid. Elution with increasing percentages of methanol in methylene chloride yielded a series of fractions that were analyzed by gas chromatography. For example, the developed elution program shown in Table 1 produced a successful separation of SE groups 1–5. The higher-substituted, but less polar SE, groups eluted first followed by the increasingly polar lower groups. It was apparent that the presence of three or four octanoyl groups greatly reduced the polarity of the total sucrose molecule, even though four or five of the original hydroxyls were still present. By contrast, group 2 SE eluted over a range of polar fractions. The small increases in the percent of methanol were selected on purpose in order to obtain fractions that were 100% pure dioctanoyl sucrose esters. As shown by the GC data, this objective was achieved. The elution scheme could be modified to obtain pure trioctanoyl SE. Individual groups of monooctanoyl, dioctanoyl, and trioctanoyl sucrose esters could now be tested for biological activity against whiteflies and aphids. At this time, heptanoyl sucrose esters (C_7SE), nonanoyl sucrose esters (C_9SE), decanoyl sucrose esters (C_{10}SE), and didodecanoyl sucrose esters (C_{12}SE) were also synthesized by the same

Table 2. Bioassay Results of Different SE against Tobacco Aphids

SE[a]	no. of tests	mortality[b] (%)
monoheptanoyl sucrose	1	17
diheptanoyl sucrose	3	88
triheptanoyl sucrose	2	16
water	3	5
monooctanoyl sucrose	1	11
dioctanoyl sucrose	3	88
trioctanoyl sucrose	2	27
water	3	5
mononononanoyl sucrose	1	16
dinonanoyl sucrose	2	64
trionanoyl sucrose	2	13
water	3	5
monododecanoyl sucrose	1	47
didodecanoyl sucrose	2	23
tridodecanoyl sucrose	2	15
water	3	5

[a] Tested at 1 mg of SE/mL of aqueous spray solution, mean values for number of tests shown. [b] After 24 h, standard deviations ranged from 5% to12%.

Table 3. Bioassay Results of the Total SE Reaction Product against Tobacco Aphids

reaction products[a]	mortality[b]	reaction products[a]	mortality[b]
total heptanoyl SE	95	total decanoyl SE	64
total octanoyl SE	85	control (water)	5
total nonanoyl SE	75		

[a] Tested as an aqueous dispersion at 1 mg/mL (0.1%). [b] After 24 h, mean values of two tests, standard deviation of 8–14%.

method and then separated into individual groups by SA column chromatography, as was done for the C_8SE.

Bioassays of the total SE reaction products as well as of the individual groups of SE were conducted using first the tobacco aphid and then the sweet potato whitefly. Tables 2 and 3 show the percent mortality of aphids treated by the individual sucrose ester groups and the total SE reaction products. The results (Table 2) indicated that diheptanoyl and dioctanoyl sucrose esters produced the highest percent aphid mortality. Sucrose esters of hexanoic acid (not shown) were also tested and gave low percent mortality (about 23–43%), while SE of higher aliphatic acids (C_9, C_{10}, C_{12}) produced progressively lower mortalities. It was most interesting to see (Table 3) that the total reaction SE products derived from the heptanoyl and octanoyl sucrose esters were also highly active against aphids. (In a commercial application, the use of the total reaction SE product would be more economical than SA fractions.) Thus, heptanoyl and octanoyl SE preparations, as well as their group 2 SE, are potent pesticides against tobacco aphids.

Bioassay tests with the total SE mixtures were conducted also against the adult sweet potato whitefly (Table 4). After only 2 h, assay results indicated high toxicity for all of the total sucrose ester reaction products, with the highest whitefly mortality produced by the C_8SE product. It is expected that higher concentrations (above 1 mg/mL) of the other SE products would also yield high toxicities against soft-bodied arthropods.

As the bioassay tests had established that the diacyl sucroses, such as the dioctanoyl sucroses, were the most toxic compounds against whiteflies, the next step was to determine their structures. Accordingly, efforts were first concentrated on determining the structure of the major dioctanoyl sucrose. Silicic acid fractions of the C_8SE product were selected for their high content of the

Table 4. Toxicities of Total SE Reaction Products against the Sweet Potato Whitefly

reaction products[a]	sweet potato whiteflies: no. of tests	sweet potato whiteflies: mortality[b] (%)
total hexanoyl SE	3	80
total heptanoyl SE	3	95
total octanoyl SE	3	99
total nonanoyl SE	3	92
total decanoyl SE	3	80
control (water)	3	5

[a] Tested at 1 mg/mL of aqueous spray solution. [b] After 2 h, mean values from three tests, four repititions each, standard deviation ranged from 4 to 7%.

major group 2 SE compound, and these were further subjected to a chromatotron (spinning thin-layer chromatography plate) separation to yield a fraction highly enriched in the major dioctanoyl sucrose ester. Subsequent LH-20 chromatography, using a chloroform–methanol solvent gradient (Severson et al., 1994), yielded the pure compound. Our past GC–MS experience in characterizing the SE of the *Nicotiana* species (Arrendale et al., 1990; Severson et al., 1984, 1994) proved most helpful in determining the structure of the synthetic compound. MS data showed an m/z fragment at 505, indicating the presence of only monooctanoylglucose or monooctanoylfructose fragments. This meant that the original dioctanoyl sucrose ester had one octanoyl group on each half of the sucrose molecule. This proposed structure was confirmed by subsequent NMR experiments. The literature has over a dozen references on NMR data of natural sucrose and glucose esters (Severson et al., 1985; Nishida et al., 1986; Matsuzaki et al., 1988, 1989, 1991, 1992; King et al., 1993; Ohya et al., 1994). Using these data combined with our NMR analyses, which included proton NMR, ^{13}C-NMR, broad-band decoupling, and J-resolve experiments, it was proven that this major group 2 compound was 6,6′-dioctanoyl sucrose. The proton NMR spectrum of this SE presented considerable difficulty in interpretation. The sucrose portion of the spectrum was complex, and many peaks overlapped. COSY experiments allowed connectivity for G1 to G2, G2 to G3, and G3 to G4, but G4 to G5 and G5 to G6 were confusing because of overlap with the fructose protons. The fructose proton assignments were also confused by the overlapping resonances. Broad-band proton decoupling experiments did not seem to resolve the issue. Final assignments of protons and carbons required HETCOR J-resolve experiments (Nakanishi, 1990) in which all protons were decoupled and correlated to carbon-13 resonances. The values for these correlations are shown in Tables 5 and 6.

As the next major compound in abundance in the SE product was the triacyl sucrose, it was of interest to determine the structure of the trioctanoyl sucrose ester. In addition to the 505 ion representing monooctanoylglucose or monooctanoylfructose fragments, the GC–MS data also showed a 559 ion, indicating that there were two C_8 groups on fructose or glucose. This showed that the trioctanoyl sucrose ester had one octanoyl group on one half of the sucrose molecule and two octanoyl groups on the other half, but it was not clear as to which half of the sucrose molecule had the two C_8 groups. In view of the fact that sucrose has three primary hydroxyl groups on the 6, 1′, and 6′ carbons, acylation at these positions is much more likely to occur than on the more hindered, secondary hydroxyls on the 2, 3, 4, 3′, and 4′ carbons. This was confirmed by NMR experiments that

Table 5. ^{1}H-NMR Shift (δ) Data for Major Synthetic SE

	6,6′-di-*O*-octanoylsucrose	6,1′,6′-tri-*O*-octanoylsucrose
G1	5.38	5.36
G2	3.46	3.42
G3	3.77	3.72
G4	3.27	3.26
G5	4.15	4.06
G6a	4.26	4.26
G6b	4.46	4.4
F1a	4.27	4.24
F1b	4.44	–
F3	4.71	4.76
F4	4.07	4.16
F5	3.94	3.9
F6a	4.40	4.28
F6b	4.43	4.38

Table 6. ^{13}C-NMR Shift (δ) Data for Major Synthetic SE

	6,6′-di-*O*-octanoylsucrose[b]	6,1′,6′-tri-*O*-octanoylsucrose[a]
G1	92.42	92.94
G2	71.52	71.42
G3	74.30	74.18
G4	71.43	71.26
G5	77.03	76.03
G6	66.36	62.97
F1	64.61	65.90
F2	104.80	104.00
F3	79.97	78.35
F4	72.89	72.48
F5	80.62	80.40
F6	64.74	64.54

[a] The carbonyl carbons had values of 172.8, 173.2, and 173.7 ppm for the three acyl substituents. [b] The carbonyl carbons had values of 173.7 and 173.8 ppm for the two acyl substituents.

showed the structure of the triacyl sucrose to be 6,1′,6′-trioctanoyl sucrose. The ^{1}H-NMR assignments for the sugar portion of the triester were determined by 2-D COSY experiments and are listed in Table 5. The pattern of substitution for the three ester moieties was established by the assignments of protons to the various carbons of sucrose by the downfield shift of those protons attached to the *O*-acylated carbon hydroxyl group. Connectivity between protons on adjacent carbons was easily established for the glucose and fructose portions of the molecule except for the anomeric F2 carbon, which has no connectivity to other carbons due to a lack of protons. Chemical shift values for protons on carbons containing free or *O*-acyl substituted hydroxyl groups were compared to those taken from various literature sources. They reflected and were in agreement with values of downfield shift caused by *O*-acyl-substitution. The ^{13}C-NMR assignments for the triester were determined by the normal and the multiplicity experiments (Table 6). The anomeric F2 carbon resonance appeared at 103.8 ppm and disappeared in the multiplicity experiment (confirming no hydrogens). Three resonances for carbonyl were found at 172.8, 173.2, and 173.7 ppm and also disappeared in the multiplicity experiment confirming the triacyl nature of the molecule. All 12 resonances of the sucrose structure were accounted for and could be assigned to specific carbons.

In line with the structural determinations for the dioctanoyl and trioctanoyl sucrose esters, it is most logical to assume that the structures of the monooctanoyl SE are 6-octanoyl sucrose, 6′-octanoyl sucrose, and 1′-octanoyl sucrose. Thus, the two large peaks (doublet) in the group 1 gas chromatogram probably are the 6- and 6′-octanoyl sucrose, while the smaller peak corresponds to the 1′-octanoyl sucrose that is formed

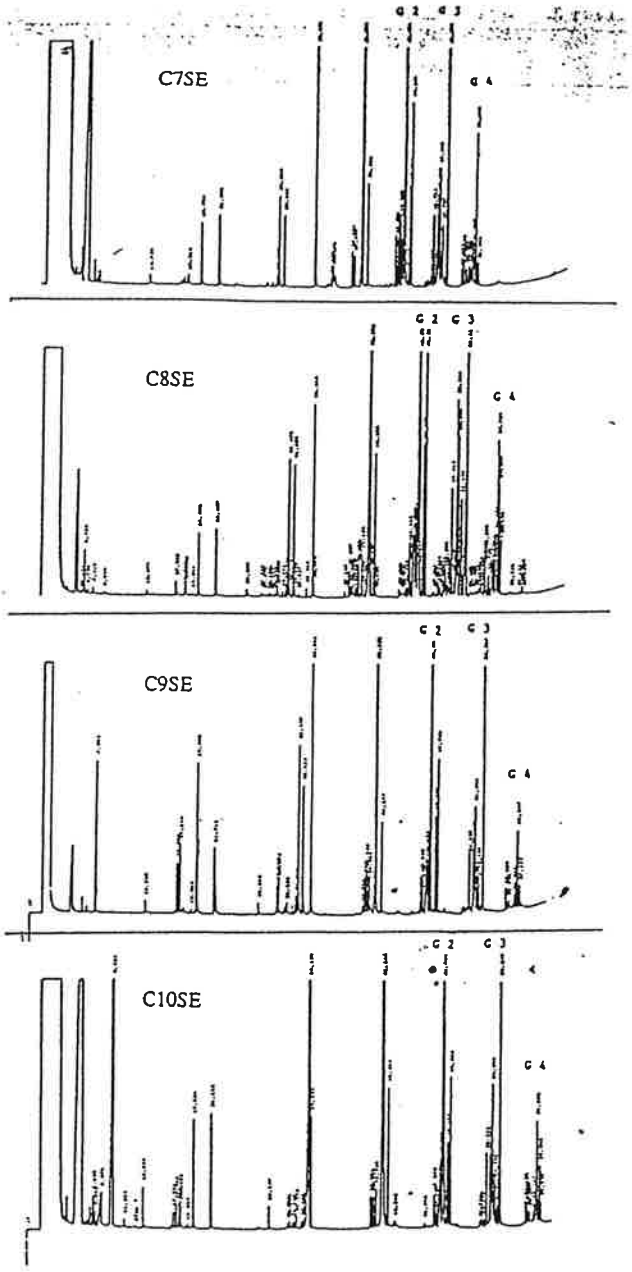

Figure 2. Gas chromatograms of heptanoyl, octanoyl, nonanoyl, and decanoyl sucrose esters products (TMS derivatives).

from the more hindered 1′-hydroxyl group. Similarly, the other dioctanoyl sucroses are probably the 6,1′ and 1′,6′ compounds. However, nature does not follow the rules of conformational stereochemistry, as most of the natural sucrose esters have acid groups on the 2, 3, and/or 4 carbon of glucose (Severson et al., 1991).

The gas chromatograms of the heptanoyl, nonanoyl, decanoyl, and dodecanoyl SE products were identical with that of the octanoyl sucroses, showing the same product distributions. As expected, higher retention times with increasing molecular weights of the SE were observed (Figure 2), that is, group 2 SE for C_{12}SE eluted later than C_{10}SE, which were later than C_9SE, etc., as expected for compounds of increasing aliphatic chain lengths. Thus, the synthesis produced the same distribution of SE for each aliphatic acid.

It was concluded that this synthetic method produced highly toxic SE products for the control of whiteflies and possibly other soft-bodied arthropods. The simplicity and reproducibility of the developed synthesis and the large quantity of toxic SE that can now be produced in a rapid manner indicate that this synthetic method should be readily adapted for commercial production of environmentally-friendly insecticides against the highly destructive whiteflies and aphids. The future of these sucrose esters appears to be bright. A patent application has been filed on the use of these SE for the control of soft-bodied arthropods. Three commercial companies have signed cooperative research and development agreements and are committing extensive funds and expertise for the testing of these compounds, and over a dozen cooperators are field testing these SE against various insects on various agricultural and ornamental crops.

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