TABLE III

Gas Chromatographic Analysis of $NaIO_4$-$KMnO_4$ Oxidized C_{22}- and C_{24}-Monoene Fractions

Acid	C_{22} (Fraction 10)	C_{24} (Fraction 11)	
	Entire oxid. mixture	Steam-volatile	Steam-nonvolatile
	%	%	%
Octanoic	......	0.5	......
Nonanoic	41.0	99.5	......
Dodecanedioic	0.5	......	......
Tridecanedioic	52.9	......	......
Tetradecanedioic	......	......	2.6
Pentadecanedioic	5.6	......	97.4

lized from acetone and the yield was 0.083 g., m.p. 145–146°.

Anal. Calcd. for $C_{29}H_{38}O_6Br_2$: Br, 24.9. Found: Br, 24.6.

Pentadecanediamide was prepared essentially according to the procedure of Shriner *et al.* (11) using 0.137 g. of pentadecanedioic acid. A 0.079-g. portion of diamide, m.p. 172–173° was obtained after recrystallization from aqueous ethanol; lit. value is 173° (12).

Anal. Calcd. for $C_{15}H_{30}O_6N_2$: C, 66.6; H, 11.2. Found: C, 66.4; H, 11.0.

Identification of the C_{22} Monoene. A 1.2-g. portion of fraction 10 was oxidized by von Rudloff's periodate-permanganate procedure (9) using 60% *t*-butyl alcohol for 24 hr. The product was worked up as usual and yielded 1.3 g. of semisolid acids. A portion of these acids was esterified, and their analysis by gas chromatography are given in Table III.

Acknowledgments

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Dialkyl Esters of Alpha-Sulfofatty Acids

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Lower olefins, especially ethylene and propylene, have been found to add to alpha-sulfofatty acids in the presence of boron trifluoride or its etherate to give dialkyl alpha-sulfofatty esters. Some of the reaction variables studied include catalyst, catalyst concentration, and solvent. The esters were obtained as colorless, low melting solids after purification by low temperature crystallization.

UNTIL RECENTLY, esters of sulfonic acids have been available only by the action of sulfonyl halides on hydroxy compounds (1), by rearrangement of alkyl sulfites (2), or by a metathetical reaction of silver sulfonates with alkyl halides (3). None of these methods is satisfactory economically for the preparation of esters of sulfonated fatty acids. Recently however the esterification of several aromatic and short chain aliphatic sulfonic acids was reported, using boron trifluoride and olefins under pressure (4, 5). Also, boron trifluoride or its derivatives are useful catalysts for the esterification of carboxylic acids with olefins, and a number of simple carboxylate esters have been prepared in this way (6).

In the present work, reactions of ethylene with alpha-sulfofatty acids for the preparation of diethyl alpha-sulfofatty acid esters were run in a 1-l., stainless steel, stirred autoclave, boron trifluoride being used as a catalyst. In general, the boron trifluoride was added to the solid alpha-sulfofatty acid and ethylene, then charged to the vessel. The reaction starts almost immediately and is slightly exothermic. The reaction temperature generally ranged from 35 to 45°C. at 500–700 psig. ethylene pressure. Uptake of ethylene usually ceased in 4 to 7 hr. at which time the reaction was essentially complete.

Some of the reaction variables such as catalyst, catalyst concentration, and solvent were investigated using alpha-sulfopalmitic acid. Table I illustrates the effect of catalyst concentration on the extent of reaction. It can be seen that a sharp break in per cent conversion occurs at a catalyst concentration of 33 mole-%. Concentrations above 33 mole-% do not affect the yield appreciably but catalyst concentrations below 33 mole-% result in markedly decreased yields.

The experiments in Table I were run in the absence of a solvent. A second series of experiments was run to determine the effect of solvent on the reaction. These are summarized in Table II which shows that a substantial lowering of yield occurs in the presence of solvents. Polymerization of ethylene is considerably higher as indicated by the polymer content of the crude ester.

Other Lewis acid catalysts which might catalyze the esterification of alpha-sulfopalmitic acid were

TABLE I

Catalyst Concentration

Run	BF_3 conc. mole-%	Conversion, %	Polymer, %	Acid value	Sap. equiv.
1	42.8	87.5	18.5	9.3	240
2	37.5	95.5	12.5	3.1	225
3	34.6	91.5	19.5	2.6	243
4	33.3	47.5	18.0	16.8	239
5	31.0	34.0	23.5	2.2	255
6	20.0	nil	......	......	......

tested under the conditions listed in Table III. No reaction was noted in any of these cases even at prolonged reaction times. Aluminum chloride in methylene chloride solvent led to extensive polymerization of the ethylene.

The reactions for the preparation of the propyl esters were run in a standard Parr hydrogenation apparatus at pressures below 60 psig. The data contained in Table IV summarizes the effect of varying catalysts and solvents on yields of ester. Propylene seems to be more readily polymerized under these conditions than is ethylene. The higher reactivity of propylene is also reflected in the fact that boron trifluoride etherate served successfully as catalyst for the reaction, although boron trifluoride was still the most effective catalyst.

The infrared spectra of diethyl alpha-sulfostearate and palmitate were determined in chloroform solution using a Perkin-Elmer Model 21 Infrared Spectrophotometer with sodium chloride optics. The carboxylate ester band appears at 5.75 μ. Simon *et al.* (7) have made assignments of bands characteristic of the ethyl sulfonate grouping from the spectra of two ethyl esters of alkyl sulfonic acids. In the spectra of diethyl alpha-sulfopalmitate and diethyl alpha-sulfostearate, bands are found at 7.29, 7.37, 8.54–8.75, 10.00, and 10.85 μ, in good agreement with Simon's assignments.

Experimental

Following are two typical examples of the experimental procedures used in the preparation of dialkyl alpha-sulfofatty acid esters.

Diethyl Alpha-sulfopalmitate. A 1-l. autoclave was charged with 168.2 g. (0.5 mole) of alpha-sulfopalmitic acid and 20.4 g. (0.3 mole) of gaseous BF_3 was tared into the vessel. Ethylene was then introduced until a total pressure of 600 psig. was obtained. This pressure was maintained for about 5 hr. The reaction was exothermic and the temperature rose to 40°C. and remained there throughout the reaction. The reaction vessel was vented and the product removed with Skellysolve F, washed thoroughly with 50% aqueous methanol, dried over anhydrous Na_2SO_4 and stripped of solvent to yield 214 g. of crude diethyl alpha-sulfopalmitate.

TABLE II

Solvent Effect

Run	Solvent	BF_3 conc. mole-%	Conversion, %	Polymer, %	Acid value	Sap. equiv.
1	none	37.5	95.4	12.5	3.1	225
2	CCl_4	37.5	34.7	29.8	79.5	279
3	CH_2Cl_2	37.5	63.5	41.5	3.5	336
4	CH_2Cl_2	54.5	80.2	37.5	8.4	314

TABLE III

Catalyst

Run	Solvent	Catalyst	Catalyst conc. mole-%	Time (hr.)	Conversion
1	CH_2Cl_2	$BF_3 \cdot Et_2O$	50.0	22	nil
2	CH_2Cl_2	$AlCl_3$	54.5	5	nil
3	none	$AlCl_3$	50.0	29	nil
4	CH_2Cl_2	$FeCl_3$	50.0	19	nil
5	none	$FeCl_3$	54.5	22	nil

TABLE IV

Diisopropyl Alpha-sulfopalmitate

Run	Solvent	Catalyst	Catalyst conc. mole-%	Time (hr.)	Temp. °C.	Press. psig.	Conversion, %	Poylmer, %
1[a]	none	$BF_3(g)$	....	4	25	40	87	66
2	CCl_4	$BF_3 \cdot Et_2O$	50.0	4	5–10	40	54	30
3	Skellysolve F	$BF_3 \cdot Et_2O$	50.0	6	5–10	40	nil	....
4	Acetone	$BF_3 \cdot Et_2O$	50.0	5	5–10	40	nil	....
5[b]	CH_2Cl_2	$BF_3(g)$	....	3	35–40	20	90	34

[a] Run in 300-ml., stainless steel, stirred autoclave, 35 psig. BF_3.

[b] Saturated with BF_3 at 6 psig.

Analysis: Sap. Equiv.: calc., 196; found, 225.
Acid Value: calc., 0; found, 3.1.

The saponification equivalent corresponds to about 13% polymer present in the crude ester, representing a 95% conversion. Two crystallizations from Skellysolve F at 0–5°C. yielded a white solid melting at 19–20°C.

Analysis: Calc. for $C_{20}H_{40}O_5S$: C, 61.18; H, 10.27; S, 8.15.
Found: C, 61.66; H, 10.40; S, 8.06.
Sap. Equiv., 196.
Acid Value, 1.0.
$n_D^{20} = 1.4525$.

Similarly diethyl alpha-sulfostearate was obtained as a white solid melting at 27–28°C.

Analysis: Calc. for $C_{22}H_{44}O_5S$: C, 62.8; H, 10.54; S, 7.62.
Found: C, 63.5; H, 10.64; S, 7.60.
Sap. Equiv.: calc., 210; found, 212.
Acid Value: calc., 0; found, 2.7.
$n_D^{30} = 1.4507$.

Diisopropyl Alpha-sulfopalmitate. A Parr hydrogenation apparatus was charged with 33.65 g. (0.1 mole) of alpha-sulfopalmitic acid and 150 ml. of methylene chloride. Gaseous BF_3 was charged to 45 psig. This dropped to 0 psig. when the mixture was agitated. Propylene was then added until a pressure of 20 psig. was obtained. This pressure was maintained for 3.5–4 hr. at 35°C. with agitation. The reaction mixture was then treated as before to yield 57.2 g. of crude diisopropyl alpha-sulfopalmitate.

Analysis: Sap. Equiv.: calc., 210; found, 318.
Acid Value: calc., 0; found, 1.7.

The saponification equivalent corresponds to about 34% polymer present in the crude ester. The crude material represents, then, about 90% conversion of the acid. Two crystallizations from Skellysolve F at −20°C. yielded a pale yellow oil.

Analysis: Sap. Equiv., 214.
Acid Value, 2.0.

Discussion

The boron trifluoride catalyzed esterification of alpha-sulfofatty acids with olefins provides a method whereby dialkyl and specifically, diethyl, esters of alpha-sulfofatty acids can be prepared easily and in high yield. The process should be readily adaptable to large scale plant production and represents the first economically feasible method of producing this class of compounds. The relatively high catalyst requirements of the reaction can probably be balanced to a large degree by reclamation of the boron trifluoride from the reaction mixture either as the gas or as addition compounds (8).

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Biochemistry of the Sphingolipids. XIV. Inositol Lipids of Flaxseed[1]

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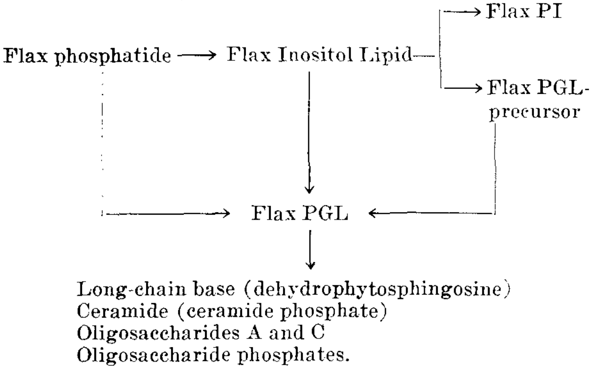
A study has been made of the inositol-containing lipids of flaxseed phosphatides. Solvent fractionation procedures have been developed for the preparation of an inositol lipid fraction from the oil-free phosphatide. By countercurrent extraction, the inositol lipid fraction was separated into a crude phosphatidyl inositol fraction and a second fraction containing long-chain base nitrogen. The phosphatidyl inositol was shown to exist as a mixed magnesium-calcium salt and evidence is presented that nitrogenous impurities (mainly phosphatidylethanolamine) may be bound to phosphatidyl inositol through a chelated salt linkage. The long-chain base fraction was shown to contain phosphatidyl inositol and two phytoglycolipids, one similar to that from corn and soybean; the other of a novel type in which the oligosaccharide portion contains galactose, arabinose and fucose. The long-chain base in flax phosphatides was shown to be dehydrophytosphingosine. It was suggested that phytoglycolipid may exist in a loose complex with phosphatidyl inositol (possibly as a chelated magnesium and/or calcium salt).

A method for the preparation of crude inositol lipid fractions from corn, soybean, and other plant phosphatides has been reported (1). The products were designated as inositol lipid fractions (corn IL, soybean IL, etc.) and contained about 80% of the original lipid-bound inositol. These materials were shown to consist mainly of phosphatidyl inositol (PI) and a second long-chain base-containing fraction which was designated as phytoglycolipid (PGL). The original lipid from which PGL was derived will be designated as PGL-precursor pending its further characterization. Unfortunately, success was not obtained in these previous studies in separating PI- and PGL-precursor on a preparative scale from the IL fractions, although a partial resolution was achieved by extended countercurrent distribution.

In the previous work, preliminary studies were made on flaxseed phosphatides with some indication of differences in the properties of the PGL obtained. A more extensive study of the inositol lipids of flaxseed was undertaken with the hope of developing a procedure for fractionating the IL in order better to characterize the constituent lipids. The present paper describes procedures for preparing flaxseed IL and separating it into PI- and PGL-precursor fractions. Also reported are procedures for the preparation of flax PGL and preliminary characterization studies on the various fractions. These studies are summarized in the following flow sheet.



Flaxseed phosphatide gave flax IL in yields comparable to those obtained from corn and soybean (20–25%). The product was a slightly colored powder which dissolved readily in benzene, chloroform, and similar solvents. Analytical data for the original phosphatide and for flax IL are given in Table I. The substantial ash content of the original phosphatide is noteworthy and caused difficulty in the attempt to prepare flax PGL by direct alkaline hydrolysis of the phosphatide. The high magnesium content of the ash is also of interest [in corn IL calcium (1.41%) predominates over magnesium (1.19%)].

Flax IL gave a strong positive anthrone test and a positive ninhydrin test. Acid degradation studies using the procedures previously reported (1) showed the presence of galactose, arabinose, mannose (weak), and a previously undetected sugar which ran on papergrams like a methyl-pentose and was eventually identified as fucose. Inositol, inositol phosphate, glycerol, and glycerol phosphate were also detected. The main nitrogenous components were found to be long-chain base and glucosamine with minor amounts of

TABLE I
Analyses of Flaxseed Phosphatides

Material	Yield	Nitrogen	LCB nitrogen	Phosphorus	Sugar (as galactose)	Ash
	%	%	%	%	%	%
Flaxseed phosphatide	100	1.02	0.08	3.29	4.53	14.0
Flaxseed IL	25	0.63	0.28	3.39	6.89	11.8[a]
Flaxseed PI	13	0.37	0.08	4.03	trace	12.8
Flaxseed PGL-precursor[b]	10	1.09	0.48	2.51	11.0	......

[a] Ca 0.65%; Mg 2.48%; Na, Fe, Ni, Zn, Si > 0.1%; Mn, Pb > 0.03% by emission spectrographic analyses.
[b] Glycerol 3.67%; inositol 15.2%.

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