soybean oil) is markedly different. When mixed, instead of sending filaments into the water, the oily phase is progressively invaded by anisotropic and isotropic forms that contain definite proportions of glycerides and phospholipids. The interpretation of this phenomenon is as follows. When water is contacted with a solution of phosphatides and glycerides, mixed double layers are formed that contain both phosphatide and glyceride molecules. Within these layers, the two types of molecules interact; the energy of interaction varies according to the proportions of the two types of molecules and passes through a maximum at ca. 70% phosphatides and 30% glycerides. The building up of the most stable mixed layer corresponds to the maximal interaction energy. Thus, any mixed layer formed spontaneously at the water surface must contain phosphatides and glycerides in the 70:30 ratio, and this has been confirmed experimentally (18). This accounts for the fact that lecithin produced by hydrating, centrifuging and drying contains appreciable amounts of glycerides.

The experimental data presented here show that water concentration and agitation in some unknown fashion affect the proportion of glycerides entrained in the hydrated gums.

Crauer (6) has reported that use of the improper amount of hydration water has a deleterious effect on the quality of both the crude gums and the degummed oils. Separations made in a small, high-speed centrifuge showed that when the gums have been properly hydrated, a compacted gum phase and a clear degummed oil fraction is obtained. Too much water yields three phases consisting of hazy, degummed oil, a free water phase, and a fluid, yellow phase due to high oil content of the gums. Too little hydration water results in dark, viscous gums and hazy oil. Thus, there is some evidence that the effects of water observed here may be analogous to those in commercial operations. Whether the effects of agitation would prevail in commercial operations is not known and requires further investigation.

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Compositions of Commercial Corn and Soybean Lecithins

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ABSTRACT

The lipid and fatty acid compositions of commercial corn and soybean lecithins were compared. The types of lipids were similar, but the proportions varied. The ratio of glycolipids to phospholipids was 0.36 for corn lecithin and 0.14 for soybean. Phosphatidylcholine and phosphatidylinositol were major phospholipids in both lecithins. In soybean lecithin, the percentage of phosphatidylethanolamine equaled that of phosphatidylinositol, but in corn, the percentage of phosphatidylethanolamine was only about one-fourth the percentage of phosphatidylinositol. High levels of phosphatidic acid in both the corn and soybean preparations indicated some degradation of the phospholipids during processing. The major differences in fatty acid compositions were a higher percentage of oleic acid and lower percentages of stearic and linolenic acids in corn compared to soybean. The lower level of linolenic acid should give corn lecithin greater resistance toward autoxidation and the development of off-flavors.

INTRODUCTION

In recent years in the U.S., soybeans have been the sole source of commercial lecithin (1). With the phenomenal growth now occurring in the demand for corn sweeteners, other products of the corn refining industry, such as corn lecithin, may become available and competitive.

The physical properties of a commercial lecithin are determined by the proportions and the fatty acid compositions of the various phospholipids and other lipids that it contains. In this study, we compared the lipids of a commercially prepared corn lecithin with the lipids from a commercial soybean lecithin.

MATERIALS AND METHODS

Materials

The samples of corn and soybean lecithins were provided by the A.E. Staley Co. of Decatur, IL. The soybean lecithin sample was a fluid type, usually ca. 65% acetone insoluble.

Silicic Acid Columns

The lipids of the crude lecithins were separated into classes

on silicic acid columns (2). The silicic acid (Mallinckrodt, 100 mesh, especially prepared for chromatographic analysis) was washed with water and methanol to remove fines and impurities. It was activated at 102 C overnight and again for 1 hr immediately before the column was prepared. The neutral lipids were eluted from the column with chloroform, the glycolipids with acetone, and the phospholipids with methanol. The percentage of each lipid class was determined in two ways—(a) by gravimetric analysis, i.e., direct weighing of aliquots from each column fraction, and (b) by gas chromatography (GC) of the fatty acid methyl esters with an internal standard. By weight, the mean recovery from chromatography of the corn lecithin sample on two silicic acid columns was 97.7% and that of the soybean sample was 97.4%. The recovery of methyl esters was 98.6% for corn and 97.8% for soybean.

Thin Layer Chromatography

Individual lipids were separated from each lipid class by thin layer chromatography (TLC) and were identified by comparing R_f values with authentic compounds (3) and by reaction with various spray reagents (4). To isolate lipids for fatty acid analysis, the lipids were chromatographed on plates coated with Silica Gel 60 H (E. Merck) 0.3 mm thick. During TLC, the lipids were protected from autoxidation by including 0.002% butylated hydroxytoluene (BHT) in the solvent systems and by spraying the plates with 0.02% BHT in petroleum ether after the plates had been removed from the chromatography tanks. The lipids were visualized by spraying with 2,7-dichlorofluorescein (0.1% in ethanol). For neutral lipids, the solvent system was petroleum ether (bp 60-68 C)/diethyl ether/acetic acid (80:20:1, v/v/v). Triglycerides (TG) and free fatty acids (FFA) were eluted from the silica gel by three extractions with diethyl ether/methanol (9:1) (5). Diglycerides (DG) were eluted twice with diethyl ether/methanol (9:1) and once with chloroform/methanol/water (50:45:5) (5).

The glycolipids were separated by TLC with chloroform/methanol/ammonia (29.3% w/v) (70:20:1). Monogalactosyldiglycerides (MGDG) were isolated from the silica gel by extracting once with chloroform/methanol (2:1), then chloroform/methanol/water (50:45:5), and finally with methanol. Digalactosyldiglycerides (DGDG) and sterylglycoside esters (SGE) were extracted with chloroform/methanol/water (50:45:5) and with methanol.

The phospholipids were separated by two-dimensional TLC. The solvent systems were chloroform/methanol/ammonia (65:35:5) in the first direction and chloroform/acetone/methanol/acetic acid/water (50:20:10:10:5) in the second. The phospholipid spots were visualized with iodine and analyzed for phosphorus in the presence of the silica gel (6). Areas of blank silica gel corresponding in size to the phospholipid spots were analyzed as controls. The recovery of phosphorus from the thin layer plates was 81.8% (SD = ±2.6) for the corn samples and 87.9% (SD = ±2.8) for the soybean samples. For fatty acid analysis of phosphatidylcholine (PC), phosphatidylethanolamine (PE) and phosphatidylinositol (PI), the phospholipids were eluted from the silica gel twice with chloroform/methanol/water (50:45:5) and once with methanol (5).

Gas Chromatography

The methyl esters of the fatty acids were prepared by treatment of the lipids with boron trifluoride/methanol according to the procedure suggested for each type of lipid by Morrison and Smith (7). The conditions for GC of the methyl esters have been described previously (3). The internal standard was methyl heptadecanoate.

RESULTS

Lipid Classes

Both the commercial corn and soybean lecithins contained a large proportion of carrier oil, neutral lipids. Corn had the largest amount, 66.8% by methyl ester weights, compared to 48.2% for soybean (Table I). Despite the higher proportion of neutral lipids, corn also had a higher percentage (8.8%) of glycolipids than did soybean (6.4%). The percentage of phospholipids (24.4%) of corn lecithin, however, was only ca. one-half of that of soybeans (45.5%). The ratio of glycolipids to phospholipids was higher in corn lecithin than in soybean lecithin.

The largest differences between the two methods for determining the proportions of the lipid classes appear to be within the glycolipid fractions (Table I). The methyl ester weights did not include sterylglycosides or hydroxy fatty acids from cerebrosides. Both sterylglycosides and cerebrosides gave heavy spots on TLC plates of the glycolipids from corn and soybean. The glycolipid fractions may also contain carbohydrates as contaminants (2,8) which would add to the weight determinations. Alcohol-soluble proteins, amino acids and phytic acid may account for the differences between the gravimetric and methyl ester weights in the phospholipid fractions (2,8).

Because the proportion of carrier oil (fraction I, Table I) was not the same for the corn and soybean samples, lipids were compared within each lipid class. In the neutral lipid class (Table II), TG made up over 90% of the neutral lipids in both samples. The percentages of FFA and DG were only slightly higher in corn than in soybean and were low, less than 3%, in both cases.

In the glycolipid fractions, the percentage of SGE in corn was almost twice that in soybean (Table III). The percentages of MGDG were about equal, but the percentage of DGDG was higher in soybean.

When corn lecithin was fractionated on a thin layer plate and the spots were analyzed for phosphorus, 22.3% (SD = ±0.4) of the total phosphorus remained at the origin. The

TABLE I

Silicic Acid Column Chromatography of Commercial Corn and Soybean Lecithins

Lipid class	Corn[a]		Soybean[a]	
	Wt[b] (%)	ME wt[c] (%)	Wt[b] (%)	ME wt[c] (%)
Neutral lipids	52.8	66.8	36.8	48.2
Glycolipids	18.4	8.8	13.2	6.4
Phospholipids	28.8	24.4	50.0	45.5

[a]Mean values from chromatography on two columns.

[b]Gravimetric.

[c]Weight of methyl esters of fatty acids determined by gas chromatography with an internal standard.

TABLE II

Lipids of the Neutral Lipid Fraction from Silicic Acid Column Chromatography

Neutral lipids	% of fraction[a]	
	Corn	Soybean
Triglyceride	91.0	92.9
Free fatty acid	2.5	1.2
Diglyceride	2.6	1.2

[a]By weights of methyl esters of the fatty acids.

compounds at the origin were not completely identified, but they were made up mainly of phytic acid and a small amount of phytoglycolipid (9). The fact that phytate was found in the crude corn lecithin was not surprising, because the lecithin was extracted from corn germ and corn germ contains 88% of the total phytate found in the corn kernel (10). From the soybean lecithin, only 7% (SD = ±0.2) of the total phosphorus remained at the origin. The phytate phosphorus was excluded from Table IV which compares the percentages of the individual phospholipids. PC was, by far, the most abundant phospholipid in both lecithin samples, representing 43.4% of the total phospholipid phosphorus in corn and 38.2% in soybean. Second was PI at 21.1% in corn and 17.6% in soybean. The only other phospholipids that were found at levels above 4% for both corn and soybean were PE, phosphatidic acid (PA) and an unknown. In the TLC solvent systems used, the unknown phospholipid had the same R_f values as the lyso compound of N-acylphosphatidylethanolamine but was not completely identified. Some degradation may have occurred during processing, because the levels of PE and PC were lower and that of PA was higher than those normally found in phospholipids isolated directly from mature corn in our laboratory. We found 63.8% PC, 7.4% PE and 1.6% PA in corn inbred H51 (11).

Fatty Acid Composition

The fatty acid compositions of the crude corn and soybean lecithins are shown in Table V. Linoleic acid (18:2) was the predominant fatty acid, and the percentages were equal in the corn and soybean lecithins. Noticeable differences between the two were lower levels of stearic (18:0) and linolenic (18:3) acids and a higher level of oleic (18:1) acid in corn than in soybean.

When the lipids were separated into classes, the same trends, lower percentages of stearic and linolenic acids and a higher percentage of oleic acid in corn, were observed in the fatty acid compositions of all the classes (Table V). However, other differences emerged. The neutral lipids of corn had a higher level of linoleic acid, as is normal for corn oil compared to soybean oil. In contrast to the oils, both the glycolipids and phospholipids of corn had lower percentages of linoleic acid and were more saturated than the soybean glycolipids and phospholipids. Soybean glycolipids had a higher level of linolenic acid.

Each individual lipid had a characteristic fatty acid pattern (Table VI), but the overall tendencies for lower stearic and linolenic percentages and higher oleic percentages in the corn lipids persisted. The characteristic fatty acid pattern of the triglycerides was indicated by a low percentage of palmitic acid and high percentage of linoleic acid. The galactosyldiglycerides were distinguished from the other lipids by higher levels of linolenic acid, particularly in soybean DGDG. The SGE had the highest percentage of palmitic acid within the corn or soybean lipids. Among the phospholipids, PC had the highest percentage of oleic acid, and PI the highest percentage of saturated palmitic acid. Within the corn phospholipids, PE had the highest level of linoleic acid. We have found the same characteristic fatty acid patterns for these individual lipids isolated from many different corn inbreds which varied in fatty acid composition from 42 to 70% in linoleic acid (11).

DISCUSSION

We have analyzed only one sample of crude corn lecithin and one of crude soybean lecithin. Changes in the relative proportions of the lipids could occur or could be made by changing the processing conditions. The amount of carrier oil or triglycerides, e.g., could be adjusted easily. Elimination of some of the phytate in the corn lecithin may be desirable, because phytate binds zinc, iron, magnesium, and calcium and decreases the nutritional availability of these important minerals (10).

The physical properties, particularly the emulsifying properties, of corn lecithin may differ slightly from those of soybean lecithin because of the higher proportion of glycolipids to phospholipids in the corn lecithin. The emulsifying properties of soybean lecithin have been improved by various treatments (12). Alcohol fractionation has increased the ratio of PC to PE. Enzymatic hydrolysis, acetylation or hydroxylation of the phospholipids have increased the oil-in-water emulsifying properties of soybean lecithin. Corn lecithin could also be modified by these

TABLE III

Lipids of the Glycolipid Fraction from Silicic Acid Column Chromatography

Glycolipids	% of fraction[a]	
	Corn	Soybean
Sterylglycoside ester	34.2	18.6
Monogalactosyldiglyceride	9.3	7.2
Digalactosyldiglyceride	15.6	23.7

[a]By weights of methyl esters of the fatty acids.

TABLE IV

Fatty Acid Compositions of Lipids of Commercial Corn and Soybean Lecithins

Phospholipid	Corn[a]	Soybean[b]
	% of total lipid P[c]	
N-acylphosphatidylethanolamine	2.9 ± 0.5	2.0 ± 0.2
Unknown	5.6 ± 0.5	12.8 ± 0.2
Phosphatidylethanolamine	4.8 ± 0.4	17.3 ± 0.2
Phosphatidylglycerol	2.0 ± 0.5	1.2 ± 0.1
Phosphatidic acid	15.1 ± 0.6	8.4 ± 0.1
Phosphatidylcholine	43.4 ± 2.5	38.2 ± 0.5
Phosphatidylserine	1.5 ± 0.9	0.5 ± 0.1
Lysophosphatidylethanolamine	tr	0.4 ± 0.1
Phosphatidylinositol	21.1 ± 1.9	17.6 ± 0.2
Lysophosphatidylcholine	3.5 ± 0.1	1.5 ± 0.2

[a]Mean ± SD of samples from 6 TLC plates.
[b]Mean ± SD of samples from 4 TLC plates.
[c]Phosphorus at origin was not included. See text.

TABLE V

Fatty Acid Compositions of Corn and Soybean Lecithins[a] and the Lipid Class Fractions from Silicic Acid Columns[b]

	Fatty acid compositions (mol %)				
	16:0	18:0	18:1	18:2	18:3
Lecithin					
Corn	17.7	1.8	25.3	54.2	1.0
Soybean	17.4	4.0	17.7	54.0	6.8
Neutral lipid					
Corn	13.1	1.8	25.8	58.4	0.9
Soybean	11.8	4.2	24.7	52.1	7.2
Glycolipid					
Corn	34.2	2.3	18.6	42.6	2.4
Soybean	24.2	4.9	10.8	48.6	11.5
Phospholipid					
Corn	22.8	1.5	26.5	48.5	0.7
Soybean	21.4	3.8	12.0	57.0	5.8

[a]Mean of 4 determinations.
[b]Mean of 6 or more determinations.

TABLE VI

Fatty Acid Compositions of Lipids of Commercial Corn and Soybean Lecithins

Lipid	Fatty acid composition (mol %)[a]				
	16:0	18:0	18:1	18:2	18:3
Triglyceride					
Corn	12.2	2.0	25.7	59.2	1.0
Soybean	11.4	4.3	25.2	51.9	7.2
Free fatty acid					
Corn	37.1	4.1	23.8	34.0	1.0
Soybean	31.6	8.5	16.7	39.0	4.1
Diglyceride					
Corn	27.0	2.5	25.7	44.0	0.8
Soybean	24.8	6.9	16.5	46.6	5.2
Monogactosyldiglyceride					
Corn	20.5	3.3	23.1	46.6	6.5
Soybean	23.8	5.4	16.9	46.0	7.9
Digalactosyldiglyceride					
Corn	21.0	2.5	15.8	55.5	5.2
Soybean	15.7	4.8	10.2	47.7	21.6
Sterylglycoside ester					
Corn	54.9	3.1	15.1	26.1	0.8
Soybean	38.7	6.9	12.2	37.0	5.2
Phosphatidylethanolamine					
Corn	23.9	1.8	21.6	52.1	0.6
Soybean	23.2	2.6	11.6	57.1	5.5
Phosphatidylcholine					
Corn	21.7	1.7	31.0	45.0	0.6
Soybean	15.5	4.0	14.5	60.3	5.6
Phosphatidylinositol					
Corn	33.8	1.5	18.5	45.6	0.6
Soybean	35.5	6.9	7.8	44.3	5.4

[a]Mean of 4 determinations.

various processes to form the special lecithins that are used in food, medicine and industrial products (13).

We do not know of any other recent, quantitative study of the lipids of commercial corn lecithin. Our data on the relative proportions of phospholipids in soybean lecithin agree, except for PE, with the results obtained by Erdahl et al. (14) on Azolectin (Associated Concentrates, Woodside Long Island, NY) but show larger differences when compared with the percentages of phospholipids in soybean lecithin prepared in West Germany (12). The soybean lecithin papers did not include fatty acid data.

The stability of commercial lecithins depends on their contents of prooxidative and antioxidative compounds and on their constituent fatty acids. Linow and Mieth (15,16) found that the antioxidative properties attributed to lecithins were not due to the phospholipids but probably to tocopherols extracted with the carrier oil. Oil-free lecithin was found to be more susceptible to oxidation than commercial lecithin which contained carrier oil.

When the unsaturated fatty acids of soybean lecithin are hydrogenated, the resulting product has a lighter color, shows greater resistance to oxidative rancidity and possesses less odor and flavor than unhydrogenated lecithin. However, the hydrogenated soybean product has poorer emulsifying properties than the natural form (17). The major differences that we found in the fatty acid compositions of the corn and soybean lecithins were a higher percentage of oleic and lower percentages of stearic and linolenic acids in corn compared to soybean. The lower level of linolenic acid in corn should be an advantage for corn lecithin over soybean lecithin, because the triunsaturated linolenic acid oxidizes readily to produce off-flavors (13,18).

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