Sunflower Lecithin and Possibilities for Utilization

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Sunflower lecithin is an important product in countries producing large amounts of sunflower oil. Due to its high phosphatidylcholine and essential fatty acid contents, it can be well utilized as an additive in food and feedstuffs. After refinement and fractionation, its utilization in food products and cosmetics can be greatly increased and further extended after appropriate modification. Utilized as an additive in the feedstuff to piglets and porklings, it results in higher bodyweight and shortened breeding and fattening periods. It is also suitable for adjusting the energy level of broiler feeds and, owing to its choline content, the use of synthetic choline chloride can be eliminated.

KEY WORDS: Acylation, enzymic hydrolysis, fractionation, sunflower lecithin.

Lecithin can be produced from any crude vegetable oil, but because of the huge quantities of soybeans grown and processed and owing to the relatively high percentage of phosphatides in soybean oil practically all over the world, soybean oil is the principal commercial source of natural and modified lecithins. In Hungary, sunflower is the major oilseed crop, representing about 80% of total oil crop production. Thus, sunflower seed must be considered as a potential source of lecithin.

Surface activity of sunflower lecithin is generally not considered different from that of soybean lecithin. While a lot of data have been published on soybean lecithin, the phospholipid and fatty acid composition of sunflower lecithin has not received serious attention. Distribution of the main phospholipid components of sunflower lecithin appears to be rather similar to that of soybean lecithin (1–3). Sunflower phospholipids, just like soybean phospholipids, seem to be more saturated than their corresponding oils (3,4).

Comparison of the available data shows no significant difference between soybean and sunflower lecithins, but it points to poorer surface activity of the latter. One reason that users are reluctant to apply sunflower lecithin may be that it is more pasty than natural soybean lecithin and is, consequently, more difficult to handle.

To solve this problem and to make use of the similarities between the two lecithins, we applied the following recommended modifications (5): fractionation with alcohol, acylation and partial hydrolysis with phospholipase A_2 (6).

EXPERIMENTAL PROCEDURES

Fractionation. This consisted of admixture of the raw material and an appropriate dilution of alcohol (30 min); sedimentation (60 min); separation of the two layers; and vacuum distillation in a rotary evaporator.

Enzymic hydrolysis. Phospholipase A_2 was a NOVO (Bagsvaard, Denmark) product obtained from porcine pancrease (Lecithin 10L). Sunflower lecithin gums with different water content were modified with a wide range of phospholipase A_2 levels, increasing the temperature by increments of 5 at 5°C from 40 to 90°C. Reaction time varied between one and five hours.

Acylation. Sunflower lecithin gum was acylated with 1, 1.5 and 2 mol equivalent of acetic anhydride based on phosphatidylethanolamine (PE) content. Prior to acylation, potassium hydroxide was added to the gum to neutralize acetic acid generated during the reaction. Acylation was carried out at 60°C for 1 h. After the reaction mixture was dried in vacuum, the reaction rate was examined by two-dimensional thin-layer chromatography (TLC) (phosphomolybdic acid and ninhydrine).

Analytical procedures. Acid value, acetone-insoluble content and moisture content determinations (7), as well as fatty acid composition by gas–liquid chromatography (GLC), two-dimensional TLC (8,9), phosphatidylcholine (PC) content determination [Boehringer Ultraviolet Method (10)], viscosity measurement (Haake CV 100 Karlsruhe, Germany), stabilizing effect on oil/water (o/w) emulsions (11) were all determined as described elsewhere.

RESULTS AND DISCUSSION

Fractionation. Ethyl alcohol and/or ethyl alcohol–water mixtures were found to be favorable for the fractionation of sunflower lecithin. The results of one of our fractionation experiments are collected in Table 1. Sunflower lecithin containing 73% phosphatide was fractionated with 500 wt% ethyl alcohol at 45°C. An extract containing 60% phosphatide was obtained in 34.5% yield, while the PC content of the lecithin increased from 41 to 65%, and the linoleic acid content was as high as 70%. The color of the pasty product was lighter than the starting material. In

TABLE 1

Sunflower Lecithin Fractionation by Ethyl Alcohol

	Starting material	Extract	Sunflower oil[a]
Phosphatide content (%)	73	60	
Yield (%)	—	34.5	
Distribution of phosphatide components (%)			
Phosphatidylcholine	41	65	
Phosphatidylethanolamine	17	10	
Phosphatidylinositol	23	3	
Phosphatidic acid	3	3	
Phosphatidic acid	3	3	
Other phosphatides	16	19	
Fatty acid composition of phosphatide moiety (%)			
Palmitic acid	16.9	13.2	6.0
Stearic acid	5.4	4.3	4.0
Oleic acid	8.6	10.1	20.0
Linoleic acid	66.9	70.3	67.0
Other fatty acids	2.2	2.1	3.0

[a]Average value.

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TABLE 2

Sunflower Gum Fractionation by Ethyl Alcohol

	Starting material	Extract (I)	Extract (II)
Phosphatide content (%)	62	87	58
Yield (%)	—	14	21
Distribution of phosphatide components (%)			
Phosphatidylcholine	41	63	77
Phosphatidylethanolamine	17	3	16
Phosphatidylinositol	23	15	6
Phosphatidic acid	3	2	2
Other phosphatides	16	17	1
Fatty acid composition of phosphatide moiety (%)			
Palmitic acid	16.9	14.4	13.5
Stearic acid	5.4	3.7	4.5
Oleic acid	8.6	9.5	10.5
Linoleic acid	66.9	70.4	69.3
Others	2.2	2.0	2.2

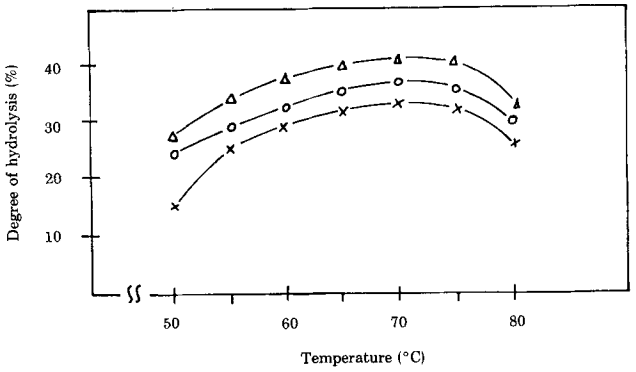

FIG. 1. Temperature dependence of hydrolysis of sunflower lecithin as a function of water content in the gum: —△— 1600 IU enzyme/100 g phosphatide, 72.0% water in the gum; —○— 1050 IU enzyme/100 g phosphatide, 70.0% water in the gum; —x— 1600 IU enzyme/100 g phosphatide, 50.0% water in the gum.

practice, the starting material, lecithin, may be replaced by crude gum. The results of an experiment carried out with gum are presented in Table 2. To a gum containing 80% water, 200 wt% alcohol was added in two steps (100 + 100%) at 45°C. After addition of the first (100%) portion, the upper layer contained 14% phosphatide of the gum. After evaporation, a light granular product with 87% phosphatide content was obtained, 63% of which was PC.

The second load of alcohol resulted in a light-colored pasty extract with 58% phosphatide content. PC increased to 77%, *i.e.*, it was enriched in the extract.

Modifications with phospholipase A_2. There are no exact data in the literature on the required reaction conditions for this lipase, *i.e.*, enzyme level has not been specified, reaction time and temperature are rather varied. In addition, some parameters prescribed cannot be realized on an industrial scale, *e.g.*, maintaining pH at 8 and optimum enzyme level would require the addition of alkali, the residue of which would increase impurity, and soaps formed from the hydrolyzed free fatty acids might cause some defect in the taste.

In summarizing our results, we have found that, in the range of enzyme levels and temperatures studied, the hydrolysis of 2-position fatty acids is catalyzed by phospholipase A_2 without pH adjustment. High enzyme levels, *i.e.*, above 6,000 IU/100 g phosphatide, lead to a high degree of hydrolysis and the generation of unwanted, highly decomposed substances. At these enzyme levels, no temperature dependence of the reaction could be observed. In contrast to some publications that recommended 40–50°C for the temperature of operation, in our experiments the optimum temperature of the enzyme was 70–75°C (Fig. 1).

The effect of water content of the gum on the degree of hydrolysis is rather significant. As is shown in Figure 1, the higher the water content, the more advantageous the specific enzyme requirement, *i.e.*, the same degree of

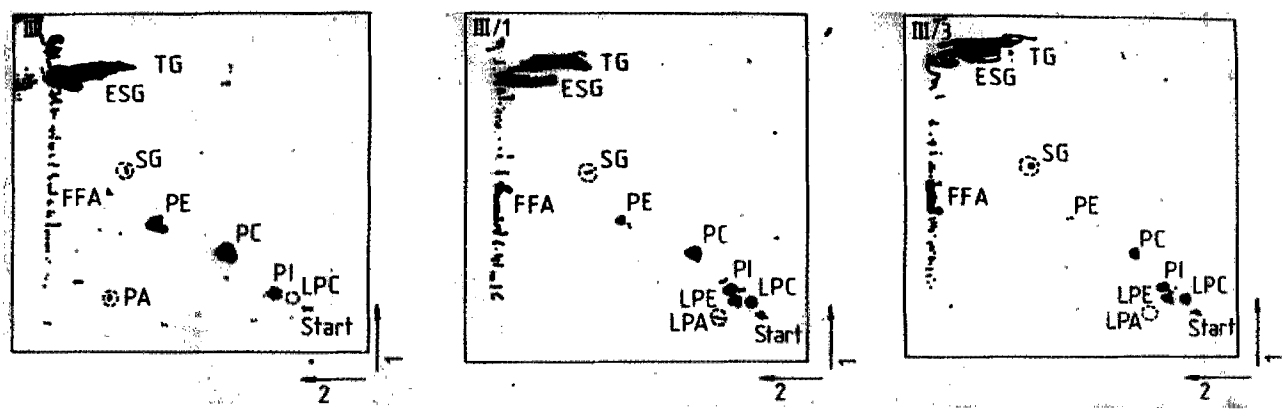

FIG. 2. Two-dimensional thin-layer chromatograms of natural and partially hydrolyzed sunflower lecithins. Silica Gel 60 (Merck, Darmstadt, Germany); solvent systems (1) chloroform/methanol/7N ammonia (65:30:4, vol/vol/vol); (2) chloroform/methanol/acetic acid/water (170:25:26:6, by vol); detection with phosphomolybdic acid. A = Natural sunflower lecithin; B = partially hydrolyzed sunflower lecithin (reaction time = 1 h); C = partially hydrolyzed sunflower lecithin (reaction time = 3 h). Abbreviations: TG = triglycerides; ESG = esterified sterol glycoside; FFA = free fatty acids; SG = sterol glycoside; PE = phosphatidylethanolamine; PC = phosphatidylcholine; PI = phosphatidylinositol; PA = phosphatidic acid; LPC = lysophosphatidylcholine; LPE = lysophosphatidylethanolamine; LPA = lysophosphatidic acid.

TABLE 3

Hydrolysis Degree (%) of Total Phospholipids and Phosphatidylcholine in Sunflower Lecithin[a]

Component	Reaction time 1 h	3 h
Total phospholipids		
Calculated from AV[b]	30.4	36.0
Calculated from AI[c]	30.7	34.2
Phosphatidylcholine	35.5	67.7

[a]The results are average values of four trials of hydrolysis from different starting materials.
[b]AV = acid value.
[c]AI = acetone-insoluble portion.

TABLE 4

Viscosity of Partially Hydrolyzed Sunflower Lecithins[a]

Reaction time (h)	Viscosity (Pa.s) sample no. 1	2	3	4
1	10-2.5[b]	10-2[b]	100-3	150-4
3	16-0.3	200-0.1	150-10	200-12

[a]Measurements made at 50°C; speed of rotation = 0-2400 s^{-1} in Haake CV 10 viscosimeter.
[b]Samples exhibited Newtonian fluid.

hydrolysis can be achieved by reducing the amount of enzyme and increasing the water content of the reaction mixture. Naturally, prior to application, conditions must be optimized, and the costs of large-scale enzyme application and higher energy requirement for evaporation should be taken into consideration as well. Substrate specificity of the enzyme was different for the individual phospholipids. As shown in Figure 2, PE was hydrolyzed first. The rate of hydrolysis of PC is lower, but after a 3-h reaction time, the degree of hydrolysis is estimated to be 60–70%. Phosphatidylinositol seems to be more or less resistant to hydrolysis. Because of the high degree of hydrolysis of the two main phospholipid components, only a 3-h reaction time (or less) was studied in detail. Quantitative results attained in the degree of hydrolysis are shown in Table 3. Hydrolysis of the total amount of phospholipids is not much dependent on the reaction time. But, in the case of the 3-h reaction, hydrolysis of PC was about twice as high as that of the total amount of phospholipids.

Fatty acid composition was determined from acetone-insoluble and soluble portions of sunflower lecithin before and after hydrolysis (Fig. 3). Compared with sunflower oil, fatty acid saturation is higher in phospholipids. In the starting material (0 h), palmitic acid content is higher (by 10%) and oleic acid content is lower (by 10%) in the acetone-insoluble portion than in sunflower oil. In the acetone-insoluble portion of partially hydrolyzed lecithins, unsaturated fatty acid content (mostly linoleic acid) decreased, and at the same time, saturated fatty acid content (palmitic and stearic acids) increased. Therefore, linoleic acid is predominantly bound in position 2, and palmitic and stearic acids are bound in position 1. The distribution of oleic acid is not characteristic.

Viscosity results are shown in Table 4. Because the samples were soft but not fluid at room temperature, measurements were made at 50°C. Compared with natural sunflower lecithin, which maintains plasticity even at 50°C, partially hydrolyzed samples proved to be fluid at this temperature. This improvement in viscosity seems to offer promising results in the utilization of sunflower lecithin. Emulsifying properties of partially hydrolyzed samples were measured in o/w emulsions (11). To ascertain whether the procedure could be reproduced properly, we compared our measurements of a soybean lecithin sample with those of known values as well (Table 5). Table 5 shows that the emulsifying properties of the modified lecithins in o/w emulsions improved with increasing hydrolysis. Comparison of the results attained with Emulfluid E (Lucas Meyer, Hamburg, Germany) showed that the samples, obtained by the 3-h hydrolysis, approached or exceeded the values of partially hydrolyzed soybean lecithin.

Acylation. Primary amino groups in lecithin, *i.e.*, in PE, can be acylated. Generally in practical applications acetic anhydride is used, and the procedure improves the fluidity

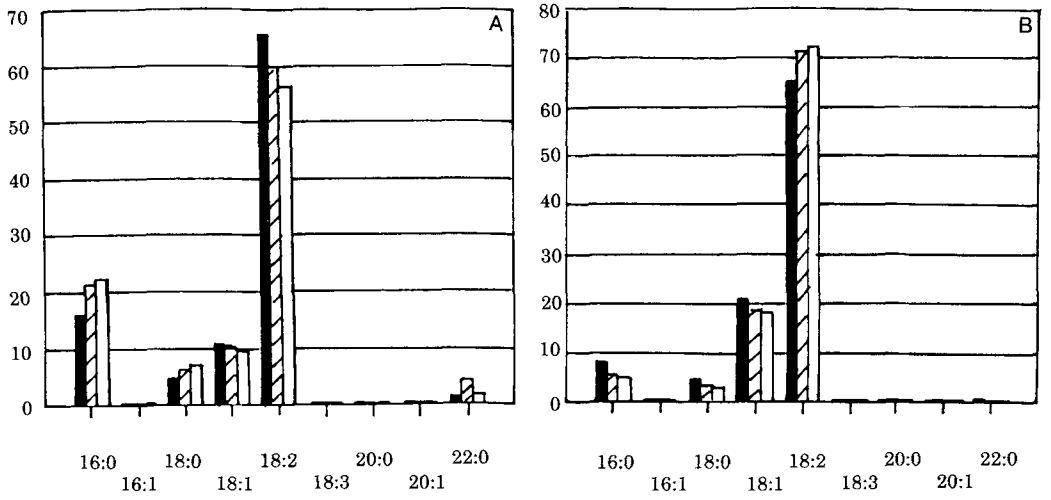

FIG. 3. Changes in fatty acid composition (%) during hydrolysis. A = Acetone insoluble portion; B = acetone soluble portion. ■ (0 h); ▨ (1 h); □ (3 h).

TABLE 5

Emulsifying Properties of Partially Hydrolyzed Sunflower Lecithin in Comparison with a Soybean Lecithin Sample[a]

Reaction time (h)	1-R[b]	R-10[c]	R-60[d]
1	50–60	1–3	4–11
3	80–240	1–2	4–10
Emulfluid E[e]	110	1	4
Emulfluid E[f]	120	1	5–8

[a]Emulfluid E is a partially hydrolyzed soybean lecithin product of Lucas Meyer (Hamburg, Germany). Values indicate the results of four trials of hydrolysis from different starting materials.
[b]1-R: Time (s) of the first separation observed visually.
[c]R-10: Volume (mL) separated in 10 min.
[d]R-60: Volume (mL) separated in 60 min.
[e]Data measured by the authors.
[f]Data as indicated by product sheet.

TABLE 6

Emulsifying Properties of Acylated Sunflower Lecithin in Comparison with a Soybean Lecithin Sample[a]

Mol Ac_2O/PE	1-R	r-10	R-60
1	70–100	1–2	3–5
1.5	80–100	0.5–2	3–11
2	60–90	0.5–1	4–7
Emulfluid A	100	1	10

[a]Emulfluid A is an acylated soybean lecithin product of Lucas Meyer (Hamburg, Germany). The values indicate the results of three trials of acylation at each acetate anhydride level.

and water dispersibility of lecithin as well as enhances its o/w emulsifying properties.

From the decrease of PE and the increase in acetyl PE spots, conversion was estimated to be approximately 40, 50 and 60% after reaction with 1, 1.5 and 2 mol equivalent acetic anhydride, respectively (Fig. 4). Although conversion increased with the increase of acetic anhydride content, the amount of potassium acetate generated may limit the acceptable quantity of the acylating agent. In a commercial product produced by acylation, the KOAc content is limited to 2%. In the case of sunflower lecithin, under the conditions applied, this value can be maintained by using 1.5 mol equivalent Ac_2O as the acylating agent. Considering the consistency of the samples obtained, the viscosity values were about 200 Pa.s at 25°C, except for one sample, which ran as low as 8.5 Pa.s and was highly fluid. The emulsifying properties of acylated sunflower lecithins were measured in o/w emulsions (11), and the results obtained are given in Table 6. The values obtained are promising because the emulsifying properties of acylated sunflower lecithin approach those of soybean lecithin, which was modified under similar conditions. Best results were obtained by using 1.5 mol acetic anhydride calculated for PE content, which may be optimal regarding the potassium acetate level as well.

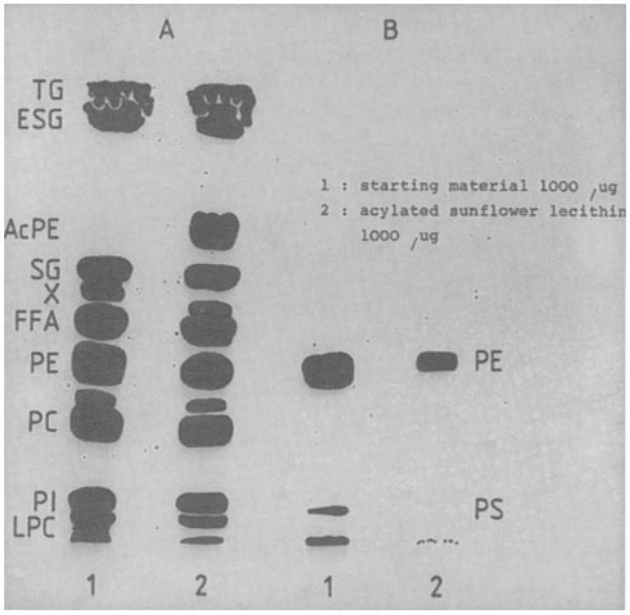

FIG. 4. Acylation of sunflower lecithin. Reaction conditions: 1.5 mol anhydride based on phosphatidylethanolamine content (dosage of KOH prior to acylation). Time: 1 h. Thin-layer chromatography: Silica Gel 60; solvent, chloroform/methanol/7N ammonia (65:30:4, vol/vol/vol); detection with (A) phosphomolybdic acid, (B) ninhydrine. 1: starting material (1000 µg); 2: acylated sunflower lecithin (1000 µg). Abbreviations: TG = triglycerides; ESG = esterified sterol glycoside; SG = sterol glycoside; AcPE = *N*-acetyl-phosphatidylethanolamine; FFA = free fatty acids; PE = phosphatidylethanolamine; PC = phosphatidylcholine; PI = phosphatidic acid; LPC = lysophosphatidylcholine; PS = phosphatidylserine.

Utilization of crude lecithin. Considering its wide range of possible applications and the substantial amounts of lecithin produced domestically, after consultation with industrial experts, the following methods of utilization and potential commercial introduction have been studied: (i) direct utilization and (ii) application after fractionation and/or modification.

Application of lecithin by addition to sunflower meal. By this method, after separation from sunflower crude oil, the gum is passed through a buffer tank and pumped into the upper section of the toaster. The amount of gum added that is related to meal is generally 2.5%, which increases the lipid content of the meal by approx. 1.0%. Although this method facilitates the utilization and marketing of lecithin, reduces meal dustiness and increases to some extent the nutrient value of the meal, it also has a drawback: lecithin can be marketed only at the price of sunflower meal.

Utilization after drying. After the drying of the sunflower gum, a pasty product with approx. 55–70% of phosphatide content is obtained. The consistency of the product can be modified, however (as in the case of other lecithins *e.g.*, soy lecithin), by the addition of organic or inorganic additives (fatty acids, oils). The products "adjusted to" about 60% phosphatide content become fluid (max. 100 Pa.s viscosity).

Sunflower lecithin is applied for the time being mainly as an additive in the feeds of poultry and pigs, but it is also utilized by the food industry and in other manufacturing.

Utilization as a source of feedstuff. A particularly important aspect of utilization is to adjust the energy

content and increase the biological value of feedstuffs (12,13). The necessary energy level is ensured by adding plant phosphatides, in our country primarily sunflower phosphatides, in addition to other fat additives. The addition of 2% sunflower lecithin to broiler feeds led to a 4–7% increase in body weight and, consequently, to a shorter breeding period (14). The high choline content of sunflower lecithin allows the use of a vitamin premix with low choline content (500 mg/kg). The use of sunflower lecithin in the feed of laying hens was also favorable. It resulted in 5–6% higher egg yields (15). Average egg mass and solidity of the shells also increased (54–56 g/egg).

Sunflower lecithin as an additive in pig feeds. Kanyó (16) found that 3–4% sunflower lecithin increases the productivity of sows, leads to body-weight increase in piglets and porkers and produces higher fodder and protein utilization. It reduces the periods of breeding and fattening (by 7.4%), improves slaughter results, the quality of meat and favorably affects the calcium and vitamin A demand of the animals. In spite of a 3.8% decrease in the amount of feedstuff and 1.5% decrease in protein applied, body weight increased from 444 to 462 g/d. During pregnancy, body weight increased from 47 to 51 kg, and the average progeny from 8.8 to 9.2 (16,17).

Sunflower lecithin as an additive to cattle feeds. For this purpose, one of our vegetable oil plants produces sunflower meal with 10% phosphatide content, but no detailed analytical data are available on the nutritional values of this product.

Utilization in food and medicinal preparations. Owing to its composition and multifunctionality, sunflower lecithin can also be utilized as a food additive. For its emulsifying properties and viscosity-reducing effect, it is currently used in chocolate production (0.5%). It is also suitable for the preparation of paramedicinal products (in the form of aromatic aqueous or alcoholic emulsions or suspensions).

In summary, so far we have had favorable experiences in utilizing natural sunflower lecithin, both in feed and food products. Utilization and application of purified and modified sunflower lecithins are being tested on industrial scale. The production of food-grade sunflower lecithin started in Martfü (Hungary) this year.

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