

☼ Sunflower Lecithin

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ABSTRACT

Because of the increased domestic production of sunflower seed oil, by-products of oil processing such as meal and lecithin will be in greater supply. Lecithin content varies according to the type of sunflower seed produced. Removal of this material is greatly affected by seed condition and processing conditions. Conditions which favor optimal removal of phospholipids are also those for optimal oil quality. This review will cover some of the properties and processing details of lecithin production.

The increase in production of sunflowers in the U.S. to slightly over 5 million acres in 1979 has increased the domestic availability of the oil and by-products of sunflower seeds.

Although sunflower lecithin currently is not used to any great extent in this country, as sunflower oil production is increased, the availability and, consequently, the use of lecithin will increase. The phospholipid content of sunflower seed oil varies from 0.5 to 1.0%; about half is extracted with the oil during processing (1). The four major phospholipids in sunflower seed oil—phosphatidylcholine (lecithin), phosphatidylethanolamine (cephalin), phosphatidylinositol and phosphatidic acid—make up 52.0, 19.7, 26.0 and 2.2%, respectively, of the phospholipids in the high oil varieties (2).

Previous work by Russian investigators has shown that the treatment of seed before oil removal and the conditions of processing can have decisive effects on the quality, quantity and ease of removal of phospholipids from the oil (1). Drying is the first important step in processing, and seed dried to a moisture below 9.5% can be stored for extended periods without resulting in oil deterioration (3). Studies on an open pollinated, high oil variety, VNIIMK, have shown that for optimal phospholipid quality and low nonhydratable phospholipid content, temperatures for drying seed to 7% moisture should be 70-75 C for unripe seed which reached physiological ripening (the 26th day from the end of flowering) or harvest ripening (the 35th day from the end of flowering), 75-80 C for ripe, field-fresh seed (the 56th day from the end of flowering), and 85-90 C for stored ripe seed. Conversion of phospholipids into the oil and reduction on nonhydratable phospholipids was most effective with steam heating for drying (1). The amount of stearines and tocopherols extracted with the oil was increased with steam conditioning of the seed (1). Further studies have shown that the longer the storage period of seed at 6% moisture and 80% relative humidity, the lower the content of phosphatidic acid and cephalin and the higher the content of lecithin in the seed (4).

Phosphatides are removed through hydration or degumming. However, removal is not total, for a fraction of the phosphatides are nonhydratable. Litvinova et al. (5) separated hydratable and nonhydratable phosphatides by dialysis and determined that the nonhydratable were nonlipid in character, consisting of acidic forms of phosphatides, lyso-derivatives, complex glycolipids, metal salts or acidic forms of phosphatides, and compounds of phosphatidic and polyphosphatidic acids with sterols and aliphatic alcohols.

The moisture content of the pressed or extracted oil during storage sometimes affects the degree of ease of

degumming. Oil with a moisture content of 0.16% can develop precipitates of phosphorous containing material, thus reducing the amount of hydratable phosphatides in the oil. Lengthy holding in storage can reduce phosphatide content in the oil by 50%. As the total content of phosphatides in the oil increases, so does the ease and degree of removal. For this reason, it is important that degumming be done as soon after extraction as possible and that stored oil is dry and protected from atmospheric moisture (6).

Phosphoric acid and some of its derivatives can reduce the amount of nonhydratable phosphatides to a negligible amount, and this technique has been incorporated into the dewaxing process by a major vegetable oil manufacturer (7). Cold alkali refining followed by the addition of phosphoric acid has been used by another major producer to refine and dewax in one step (8).

Once the sludge (or foots) has been isolated, oil is removed by drying with heat at reduced pressure. Use of the powdered produce, lecithin, is hampered by its tendency to undergo oxidative deterioration. Popov et al. (9) found that removal of fat by multiple washings with acetone (5:1 to 1:1, acetone/product) produced an oil-free, dehydrated lecithin product with color and stability that were superior to those of powdered lecithin obtained from crude lecithin using commercial conditions.

In an investigation of the appropriate factor for the conversion of phosphorous to phospholipids, Chapman (2) reported that values of 30 to 31.7 have been used with "acetone insolubles" and a value of 25.5, based on an empirical formula for lecithin of $C_{44}H_{85}PO_9H$ (10).

Chapman (2) conducted a study to determine more precisely the individual phospholipid molecular weight based on fatty acid compositions and to use those results and the phospholipid composition of the oil to calculate the average phospholipid molecular weights. These results were then used to calculate a conversion factor for crude sunflower and soybean oils.

Crude oils were separated using two-dimensional thin layer chromatography to obtain separation of individual phospholipids and fatty acid composition. Once the phospholipids and fatty acid distribution was obtained, average molecular weights were calculated. The average molecular weight for soybean phospholipids was calculated to be 769.7, which results in a conversion factor of phosphorous to phospholipids of 24.8. For sunflower seed oil, the average molecular weight was 779.5, resulting in a conversion factor of 25.2.

Because the fatty acid composition of phospholipids and the composition of phospholipids in crude oils are quite different in soybeans and sunflowers, it is surprising that the average phospholipid molecular weights were so similar and yielded almost identical conversion factors (2). The results of this study indicate that % P \times 25.0 would give a more realistic value of phospholipids in crude sunflower seed and soybean oils than would a factor of 30.

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✿ A Review of Lecithin Chemistry and Glandless Cottonseed as a Potential Commercial Source

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ABSTRACT

Industrial lecithin can be fractionated as phospholipids and glycolipids after neutral lipids and protein-containing contaminants are removed. The polar lipids are very reactive and are difficult to extract and purify from oilseeds. Their purity and special properties can be improved by a number of methods including solvent fractionation, hydrogenation, sulfonation, and ethoxylation. Studies are determining the role of the polar lipids of lecithin in (a) the synthesis of triglycerides in maturing seeds, (b) the structure of biological membranes, and (c) the molecular basis of the functionality of food ingredients. Lecithin, having both polar and nonpolar groups, has high surface activity and is reactive with both oil and protein, making it an excellent emulsifying agent in food systems; lecithin also slows autoxidation and enzyme hydrolysis of fats. Cottonseed lecithin is low in linolenic acid, prevents flavor deterioration of soybean oil and can be used to stabilize sunflower oil against color change during high temperature use. Gossypol binds to lecithin in oil from glanded cottonseed economically negating it as a commercial source of this product. New cultivars producing glandless, or gossypol-free cottonseed, may have potential as commercial sources of edible lecithin.

INTRODUCTION

At present, the only vegetable oil lecithin or crude phospholipid available for commercial use is a byproduct of processing soybean oil (1-3). In the past, phospholipids were extracted from animal materials such as egg yolk, brain tissue or spinal cord (1). These sources provided only small quantities of phospholipids, most of which were used pharmaceutically. Corn lecithin was reported to have certain superior properties for food use and was also available commercially (4). Before the early 1940s, cottonseed lecithin was commercially available and had properties superior to those of soybean lecithin (5-7), but changes in oil extraction processes produced oils that contained considerable amounts of free gossypol pigments which bound to crude phospholipids and caused color and toxicity problems (8,9). Glandless cottonseed now provides a potential source of commercial oil and lecithin that is free of gossypol pigments and color and toxicity problems (9).

"Lecithin" is the commercial or popular name for a naturally occurring mixture of several phospholipids including lecithin (phosphatidylcholine) and cephalin (phosphatidylethanolamine), phosphatidylinositol and phosphatidylserine. Brian (2) gives the proximate composition of commercial crude soybean lecithin as: phosphatidylcholine, 20%; phosphatidylethanolamine, 20%; phosphatidylinositol, 20%; soybean oil, 35%; and sugars, sterols and moisture, 5%. Commercial lecithin can be further

processed to reduce oil content and bleached to improve color.

CLASSIFICATION

The most commonly used classification of lipids is an adaptation of Bloor's method by Deuel (10), in which lipids are divided into 3 groups: (a) simple lipids, which include neutral fats and waxes; (b) compound or conjugated lipids, which include phospholipids (Figs. 1 and 2), cerebrosides and sulfolipids; and (c) derived lipids, which include fatty acids, alcohols, hydrocarbons, and vitamins D, E and K. Folch (11) found that the phospholipid fraction referred to as "cephalin" consisted not only of phosphatidylethanolamine but could be separated into phosphatidylserine and one or more phosphatidylinositol compounds.

Lishkevich (12) found lecithin, or phospholipid, content of various oilseeds highest in cottonseed, followed by soybean, sunflower, flax, castor bean, and peanut seeds. He (13) also separated cottonseed phosphatides into 3 fractions: 16.5% was acetone soluble, of which 46.2% was lecithin, and 53.8% was cephalin; 76.5% was acetone insoluble, of which 53.2-59.4% was lecithin and 40.6-46.8% was cephalin; and 7.0% was benzene soluble which was almost entirely lecithin.

Most, if not all, phospholipids can exist in α - and β -forms. Daubert (14) illustrated α - and β -phosphatidylcholine, of which the α -form is optically active and the β -form is optically inactive. The β -phosphatidylcholine is not soluble in ethanol and is not extracted by the commonly used solvent systems. Daubert also illustrated the α - and β -forms of phosphatidylethanolamine and phosphatidylserine, but made no mention of phosphatidylinositol, nor of their optical activity. Tattrie (15) illustrated the α -acyl and β -acyl lysolecithins formed by the action of snake venom lecithinase A on phosphatidylcholine.

FUNCTIONS OF PHOSPHOLIPIDS

Seeds

High percentages of total phospholipids were noted in oil of cottonseed (Table I) harvested shortly (5 days) after flowering. These percentages decreased rapidly to a value of 2.4% in mature cottonseed harvested 60 days after flowering. Although the rates varied, each of the components of the total phospholipid fraction (phosphatidylcholine, phosphatidylethanolamine, phosphatidylinositol and phosphatidylserine) declined during cottonseed maturation.