Oil recovery and lecithin production using water degumming sludge of crude soybean oils

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Abstract:

BACKGROUND: Wet gums produced during aqueous degumming of crude soybean oils are currently processed to produce lecithin or added to meals to increase their nutritive value for animal feed. Oils occluded in these gums are generally not recovered or processed. In this work, three methods to recovery occluded oil and obtain lecithin from wet gums were assayed: direct extraction of oil with cold acetone (Method I), extraction after water elimination under vacuum (Method II) and by solvent partition with hexane/ethanol (Method III).

RESULTS: Higher oil yields (up to 588 g kg^{-1} of occluded oil) were obtained when water was eliminated before extraction (Methods II and III). No significant differences were observed in lecithin yields between three methods (720-807 g kg^{-1} of dried gums). Recovered oils had acidity=16.7-21.7 g kg^{-1} as oleic acid, TOTOX values $\leq$ 8.82, unsaponifiable matter=9.0-12.1 g kg^{-1}, phosphorous=87-330 mg kg^{-1}. Lecithins obtained by Methods I, II and III-hexane phase had the same purity level (610-691 g of total measured phospholipids kg^{-1}).

CONCLUSIONS: The occluded oil in soybean wet gums can be recovered, with quality and stability indexes compatible with their re-insertion in productive process, by water elimination and extraction with acetone. Lecithins can be obtained with different phospholipipid composition and diverse application fields.

Keywords: Soybean lecithin; Soybean oil, Gums; Phospholipids

INTRODUCTION

World soybean production has been estimated for 2006/2007 in 218 million tonnes (t) and therefore about 35 million t of soybean oil will be produced. More than one million t of wet gums, which contain about 260,000 t of lecithin, will be obtained in processing of soybean oil during water degumming step. These gums or sludge are a complex mixture comprising phospholipids or lecithin, oil, and minor amounts of other constituents like phytoglycolipids, phytosterols, tocopherols, and fatty acids. They have high water content that promotes a fast damage if they are not properly stored and processed. The composition and molecular structure of this heterogeneous mixture of compounds varies depending on degumming conditions of oil. [1]

Some methods to produce, purify, and fractionate lecithin from gums have been studied. In the conventional industrial process wet gums are dried under vacuum and then de-oiled with cold acetone, solvent in which phospholipids, glycolipids and related compounds are almost insoluble. [2] Partition methods with solvents to water elimination [1] and phospholipids fractionation [3] have been also proposed. Fractions with high phosphatydyl choline/phosphatydyl ethanolamine (PC/PE) ratio and fractions with high phosphatydyl inositol (PI) contents can be obtained by fractionation with ethanol. [4,5] The PC-enriched fractions have unique anti-spattering properties as oil/water (o/w) emulsifiers in margarines with low or non-salt contents and they are suitable for systems with hard water, salts and in presence of milk proteins, because PC is not flocculated by calcium and magnesium ions. PI-enriched fractions are used as water/oil (w/o) emulsifiers in the confectionery industries. Pure phophatydyl choline can be obtained by chromatographic procedures. [3,6] Alternative methods for extraction and partition of phospholipids using supercritical fluids have been developed, although they are not applied at industrial scale. [3] The advantages of these processes are the absence of

oxygen that would promotes oxidation and solvent residues with flammability risks and environmental problems.

Lecithins can be modified by chemical reactions such as acylation and hydroxylation to increase their hydrophilic properties and behave their characteristics as o/w emulsifiers. [7,8] Special lecithins can be produced by means enzymatic modifications. A_2-Phospholipase can be used to obtain lysophospholipids with o/w-emulsification properties tremendously enhanced. [8]

Soybean represent 90% of total of oleaginous harvested in Argentina and our country is third world producer of soybean behind USA and Brazil, however only some hundred of tonnes of crude and purified lecithin are monthly produced. No processed gums are fundamentally added to pellets and meals to increase their nutritive value. Argentinian soya is characterized by low protein content that is why the gum addition to meals and pellets, reduce their protein availability and increase their lipid content, making difficult their commercialization. So, the gum processing should be a solution for these drawbacks. In 2006, the installed capacity to crush soybean in Argentina was 132,000 t per day and in a short lapse of time it will reach until 160,000 t per day. A major volume of wet gums will be produced as a consequence of this increase.

On the other hand, in spite of the extended information about phospholipids obtaining from gums, nowadays there are not studies available on the recovery of the occluded oil and the evaluation of its quality indexes. It can be estimated that more than 200,000 t of occluded oil will be lost with wet gums in 2006/2007 period. Moreover the price of soybean oil registers increases with future contracts for December 2007 in Chicago Board on Trade of 803.1 dollars/t.

The aim of present study was the recovery of occluded oil and the lecithin production from wet soybean-gums. Direct-extraction methods of oil with cold acetone,

and water elimination under vacuum and by partition with hexane/ethanol, before acetone extraction, were assayed and the oil and lecithin yields were estimated. Quality indexes were evaluated for the recovered oil and the phospholipids composition was determined for oils and lecithins.

EXPERIMENTAL

Materials

Five samples of wet gums from water degumming of crude soybean oil were provided by two commercial plants in 2004 April-September period. The samples were fractionated and stored at -20 °C to prevent damages before processing.

L-α-phosphatydyl ethanolamine (PE), L-α-phosphatydyl inositol (PI), and L-α-phosphatydyl choline (PC) from soybean, and L-α-phosphatidic acid (PA) sodium salt from egg yolk lecithin with purities greater than 98% were used as external standards for phospholipids analysis. 1-Monopalmitoyl-rac-glycerol (monopalmitin, purity: 99%) was used as internal standard for polar compounds determination. Standards were provided by Sigma (Missouri, USA). Bakerbond SPE Diol (0.5 g) and Bakerbond SPE Silica Gel (1 g) disposable extraction columns (J. T. Baker, Phillipsburg, USA) were used for phospholipids and polar compounds analyses, respectively. n-Hexane, 2-propanol, and tetrahydrofuran for HPLC were provided by J. T. Baker, Phillipsburg, USA. Tetrahydrofuran was redistilled and stabilized. All other chemicals and solvents were of analytical grade.

Method I: Oil recovery and lecithin obtaining by direct extraction

First extraction was carried out with cold acetone at 0 °C in a wet gum/solvent relation 1:1.5 w/v, continuously shaking during 30 min. After rest for 15 min the extract

was separated by filtration. The residue was extracted another twice times with cold acetone (1:1, w/v) under the same conditions. The oil was recovered by elimination of the solvent in rotatory evaporator under vacuum at 40 °C and centrifugation (1,500g, 5 min) to separate oil and aqueous phase. Finally the oil was dried under nitrogen. Lecithin was obtained drying the extraction residue in a vacuum oven (125 mmHg) at room temperature. Yields for oil and lecithin were gravimetrically determined.

Method II: Oil recovery and lecithin obtaining by drying under vacuum and extraction

Wet gum was completely dried under vacuum (70 mmHg) in rotatory evaporator at 60 °C. The eliminated water was periodically monitored by weight. Oil and lecithin were obtained according to procedure indicated by Method I. Centrifugation step was eliminated because water was not present in the extraction medium.

Method III: Oil recovery and lecithin obtaining by solvent partition and extraction

Wet gum was dissolved in n-hexane (1:1 w/w) at 50 °C with magnetic stirring and then absolute ethanol was drop by drop added until steep colour change and phases separation were observed. Hexane phase (phase-A), containing phospholipids, oil, pigments, and other minor compounds and alcohol/water phase (phase-B) with phospholipids and other components, were recovered using a separating funnel. Phase-A was evaporated at 40 °C under vacuum in rotary evaporator and treated as in Method I without centrifugation, to recovery oil and to obtain lecithin (phase-A lecithin). Phase-B was evaporated at 50 °C under vacuum and completely dried in a vacuum oven at room temperature. Yields were calculated from the weights of seldom lecithin fractions and recovered oil.

Wet gums analyses

Moisture content was determined by distillation with an immiscible solvent (toluene) according to AOCS Official Method Ja 2a-46. [9] Acetone insoluble matter was evaluated by AOCS Official Method Ja 4-46. [9] This fraction basically includes phosphatides in samples free from sand, meal, and other petroleum ether-insoluble materials. AOCS Official Method Ja 3-87 was used for measure hexane-insoluble matter. [9] The percentage of occluded oil was estimated by difference (100 - % moisture - % acetone insoluble - % hexane insoluble).

Phospholipids were determined by HPLC (AOCS Official Method Ja 7b-91) [9] with photodiode array detector at 206 nm and n-hexane/2-propanol/acetate buffer pH=4.2 (8:8:1 v/v/v) as mobile phase. HPLC system was equipped with a LiChrosorb Si-60 column (250 x 4 mm, particle size: 5 μm) and an Empower 2 Software.

Recovered oils analyses

Acidity as oleic acid percentage was measured by titration with standardized ethanolic solution of potassium hydroxide and phenolphthalein as indicator (IUPAC Standard Method 2.201). [10] AOCS Official Method Cd 8-53 [9] for peroxide value (Acetic Acid-Chloroform Method) was employed to measure peroxides and other similar compounds that oxidize potassium iodide as primary oxidation products. p-Anisidine value was determined by AOCS Official Method Cd 18-90 [9] that measure the amount of aldehydes (principally 2-alkenals and 2,4-dienals) as secondary oxidation products. Unsaponifiable matter was evaluated by AOCS Official Method Ca 6a-40. [9] This fraction includes those substances frequently dissolved in oils, such as higher aliphatic alcohols, sterols, pigments, and hydrocarbons, which cannot be saponified by the usual caustic treatment, but are soluble in ordinary oil solvents.

Phosphorous content was determined by ashing the oil in the presence of zinc oxide, followed by the spectrophotometric measurement of phosphorous as a blue phosphomolybdic acid complex (AOCS Official Method Ca 12-55). [9]

A partition procedure using SPE Diol extraction columns previously described was applied for phospholipids enrichment and their separation in oils. [11] Briefly, this procedure included: (i) sorbent conditioning with 2 mL methanol, 2 mL chloroform, and 4 mL hexane; (ii) sample loading, 200 μL of chloroform/oil solution containing 50 mg of oil were injected with a micropipette; (iii) triglycerides release from the sorbent bed, accomplished by passing 2.5 mL chloroform through; and (iv) phospholipids recovery by elution with 7 mL of a solution 25% ammonium hydroxide/methanol (0.5% v/v). The phospholipids were collected into a conical vial, evaporated to dryness under nitrogen, and made up to 100 μL with mobile phase. Phospholipids were analyzed following the procedure and conditions indicated for wet gums analyses.

Polar compounds, as products of oxidation, polymerization, and hydrolysis in heated oils, were analyzed by HPSEC using monopalmitin as internal standard, after separation of non-polar compounds in SPE extraction columns with silica gel phase. [12] Columns were first conditioning with 10 mL 40-60 °C light petroleum/diethyl ether (90:10 v/v). An aliquot of 2 mL light petroleum solution containing 50 mg of oil and 1 mg of internal standard was injected in silica bed (sample solution). Internal standard was dissolved in diisopropyl ether (5mg/mL) before adding to sample solution. Non-polar fraction (triglycerides) was eluted passing 15 mL light petroleum/diethyl ether (90:10 v/v) through silica bed. Polar fraction was collected into a conical vial with 10 mL diethyl ether, evaporated to dryness under nitrogen, and then diluted with THF mobile phase. Two PLgel columns connected in series (300x7.5 mm, particle size: 5 μm, pore

size: 500 and 100 Å), a refractive index detector, and a Millennium 2010 Chromatography Manager were used.

Obtained lecithin analyses

Phospholipids were determined by HPLC using the analytical methodology indicated by wet gums.

Statistical analysis

Methods for oil recovery and lecithin obtaining were applied in triplicate. Results are expressed as mean value ± standard deviation. The differences in mean values between samples were assessed with Student's t-test, being statistically different at significance level of 5%.

RESULTS AND DISCUSSION

Composition of soybean degumming sludge

Wet gums showed high water content, in average nearly to 500 g kg^{-1}, indicating high sensibility for hydrolytic damages when they are not stored and processed under convenient conditions (Table 1). No changes in general composition, acid, iodine, and peroxide values were observed for rapeseed wet gum stored in frozen state (-20 °C) during 24 months. [13] Gums used in this study were frozen at -20 °C and carefully processed to minimize hydrolytic damages. As can be observed in Table 1, the average phospholipids content in wet gums was almost 300 g kg^{-1} and the occluded oil was estimated in approximately 250 g kg^{-1}. Gums had a low content of hexane insoluble impurities (4 g kg^{-1}) such as sand, meal and other insoluble materials. It can be observed that the composition of wet gums is variable enough (Table 1). The source of this

variability may be genetic (plant cultivar), seed quality (maturity, harvesting-caused damage, and handling/storage conditions), and oil processing variables. [14]

Yields of recovered oil and obtained lecithin

The yields for recovered oil by Methods II and III were significantly higher, 556 and 588 g kg^{-1}, respectively (Table 2). In booth methods water was eliminated before the extraction with acetone. Method II was performed with total water elimination and in Method III about 85 % of the water was eliminated. Direct extraction method showed lower oil yields and moreover centrifugation was necessary to separate oil and aqueous phase.

The lecithin yields (720-807 g kg^{-1} of dried gum) were not significantly different in three methods (Table 2). Two fractions of lecithin can be obtained by Method III being lecithin from Phase A the most abundant.

Quality indexes for recovered oils

Table 3 shows some quality indexes for recovered oils using the three studied methods. The free fatty acids in recovered oil ranged from 16.7 to 21.7 g kg^{-1} as oleic acid and no significant differences were observed between methods. The Codex Alimentarius establishes a maximum level of 0.6 mg KOH/g (3 g kg^{-1} as oleic acid) for refined oil. [15] The National Oilseed Processors Association (NOPA), in soybean oil trading rules revised in 2007, fixes for crude degummed soybean oil, maximum levels of 7.5 g kg^{-1} as oleic acid, and applies allowances between 7.6 and 12.5 g kg^{-1}. [16] However crude soybean oil can have acid values until 4.0 mg KOH/g o 20 g kg^{-1} as oleic acid [17] which are easily reduced during refining process.

Peroxide values, as a measure of primary oxidation products, were lower than 3.24 mEq/kg, and anisidine values that measure secondary oxidation compounds, lower than

4.03 (Table 3). No significant differences were observed for these indexes in recovered oils by the three methods. Total oxidation values (TOTOX values) often used in the industry, were lower than 8.82. These values combine evidence about the past history of oil (as reflected in the p-anisidine value) with its present state (as evidenced in the peroxide value). It is acceptable maintain a peroxide value of less than 4 and an anisidine value of less than 2 in the crude oil during storage. [18] For crude oils TOTOX values minor than 10 correspond to good quality oils in industrial scale. Oxidation products are reduced during blanching in refining process.

The Codex Alimentarius fixes for unsaponifiable matter a maximum value of 15 g/kg for crude soybean oils. [15] All recovered oils were adjusted to this normative for characterization (Table 3).

Phosphorous and phospholipids in recovered oils

As shown in Table 3, the phosphorous content in oils recovered by Method I was in average 87 mg/kg in accordance to the values proposed for crude degummed soybean oil (< 200 mg/kg). [16] Shipments up to 250 mg/kg are permitted with discounts. Oils obtained by Methods II and III had higher phosphorous contents than those obtained by direct extraction (Table 3). Crude soybean oils can contain more than 1,000 mg phosphorous/kg, depending of the extraction and preparation methods and values of 10-15 mg/kg are usual in refined soybean oils. [19] Phosphorous contents in order to 1-3 mg/kg can be observed in soybean oils completely refined and packaged. The phosphorous content observed in oils recovered by Methods II and III can be easily reduced during refining process by degumming. To estimate the phospholipid contents in oils, a factor of 30 usually is applied, to convert the percentage of total phosphorous to the equivalent content of phosphatides. [20] However in crude oils this factor overestimates the phospholipids and lower factors have been proposed. [21] Crude oils

contain phosphorous from another sources, such as sand and meal residues, including inorganic phosphorous that is also determined by the spectrophotometric method.

The contents and relative composition of phospholipids in recovered oils determined by the chromatographic method are shown in Table 4. Although this method has the advantage of identifying and quantifying phospholipids separately, other minor compounds (i.e. lysophospholipids), are not determined. However four major phospholipids in soybean oil can be evaluated by chromatography and the remaining fraction is relatively low. Oils recovered by Method I had phosphorous content and phospholipid average content lower than those obtained by Methods II and III. These results suggest that during direct extraction of oil, water and hydratable phospholipids would be dragged by the acetone and retained in aqueous phase then of centrifugation. Crude soybean oils have 15-30 g of phosphatides per kg; this content is reduced to 3-8 g kg^{-1} in water degummed soybean oil, and 0.03-0.45 g kg^{-1} in refined oils. [22,23] It is remarkable that all recovered oils had total phospholipids contents practically in the range accepted for degummed products. A large dispersion between samples was observed for total phospholipid contents demonstrating strong influence of wet gum composition on the phosphatide contents in recovered oils.

As shown in Table 4, the recovered oils had high relative percentage of PC (62-77 %), and low percentages of PE and PI, when they are compared with data provided in bibliography for crude soybean oils. Mounts, Abidi, and Rennick [24] informed the following relative values working on samples of crude soybean oils, obtained from standard and genetically modified varieties: 20.7-35.8 % for PE, 18.2-27.9 % for PI, 2.1-35.0 % for PA, and 25.4-49.7 % for PC. PA is the most variable phospholipid in crude soybean oil and its percentage in the recovered oils was relatively low. A water degumming step during refining process could reduce without drawback the

phospholipids in the recovered oils, provided that PC is the most easily hydratable compound, whereas PA and PI are difficultly eliminated by hydratation. Only small significant differences in the percentages of PA and PI were observed when the methods for recovery of oil were compared (Table 4). The oils recovered by direct extraction had more non-hydratable PI than those obtained by Methods II and III. Evidently, hydratable phospholipids are dragged to aqueous phase and non-hydratable PI is more easily retained in recovered oils.

Polar compounds in recovered oils

No significant differences were observed in total and individual polar compounds between the methods for oil recovery from wet gums (Table 5). Polymerized, dimerized, and oxidized triglycerides (PTG, DTG, and OTG) are used as indicators of thermal degradation (TD). Diglycerides (DG) and free fatty acids (FFA) indicate hydrolytic degradation (HD). All recovered oils evidenced a level of HD higher than it TD (TD/HD < 1). These results suggest that the storage of wet gums, before processing, under controlled conditions to reduce the hydrolytic damage, is crucial to obtain good-quality oils.

The content of total polar compounds, in the recovered oils from soybean wet gums ranged from 48.8 to 56.1 g/kg^{-1} (Table 5). These contents are only a little higher than those observed in crude sunflower oils, obtained by pressing (43.4 and 40.5 g kg^{-1}) and solvent extraction (45.3 and 38.9 g kg^{-1}). [25] These results confirm the qualification of recovered oils as good-quality products. Moreover, a treatment by water degumming could reduce polar compounds in the recovered oils. [25]

No appreciable amounts of DTG and PTG were detected in recovered oils, an expected result since polymerization due to thermal degradation occurs at temperatures

higher than those used in the methods for oil recovery. The most significant change is observed in the concentration of OTG relating to oxidative deterioration.

Phospholipids in obtained lecithins

The content and the relative composition of phospholipids in the lecithins obtained by the three methods are shown in Table 6. No significant differences were detected in total phospholipids content between Methods I, II and III (hexane phase) with values ranging from 610 to 691 g kg^{-1}. These contents include the four phospholipids more relevant in soybean: PC, PE, PI and PA. More abundant phospholipids were PC and PE in the range of 203-319 g kg^{-1} and 185-218 g kg^{-1}, respectively (Table 6). The following values have been informed in the bibliography for soybean lecithin with intermediate range of composition: PC=290-390 g kg^{-1} and PE=200-263 g kg^{-1}. However soybean lecithin with low range of composition contains 120-210 g kg^{-1} of PC and 80-95 g kg^{-1} of PE. [14]

Lecithin obtained by Method I had the higher PC content than those obtained by extraction after water elimination. PC is extracted more efficiently by acetone when no water is disposable. Lecithin obtained by extraction oil after drying in vacuum (Method II) had slightly major PA and PI contents than those obtained by Methods I and III-Phase A. Lecithin obtained by Method III from hexane phase had the highest content of PE. The results show that lecithin obtained by Methods I, II and III-Hexane phase have the same purity level but different relative compositions and could be used in different applications.

From alcoholic phase were obtained lecithin with low total phospholipids content (168 g kg^{-1}, Table 6). Moreover, the relative composition in phospholipids of this lecithin is not significantly different from those obtained from hexane phase. More studies are required to analyze the composition of the colourless product with crystalline

appearance obtained from alcoholic phase. Other components such as glycolipids, complexes carbohydrates, etc., could be recovered under profitable way.

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Table 1. Composition of soybean degumming sludges (wet gums)

Moisture ($g\ kg^{-1}$)	Acetone insoluble matter ($g\ kg^{-1}$)	Hexane insoluble matter ($g\ kg^{-1}$)	Occluded oil ($g\ kg^{-1}$)
462 ± 48	293 ± 62	4 ± 1	241 ± 15

Phospholipids							
$g\ kg^{-1}$				% Relative			
PC	PE	PA	PI	PC	PE	PA	PI
120 ± 31	68 ± 15	28 ± 0.5	43 ± 16	46 ± 2	28 ± 2	10 ± 1	16 ± 1

Table 2. Yields of recovered oil and obtained lecithin from wet gums

	Recovered oil yield		Obtained lecithin yield	
	g kg^{-1}	g kg^{-1}	g kg^{-1}	g kg^{-1}
Method	Wet gum	Occluded oil	Wet gum	Dried gum
I	104 ± 18	429 ± 71 [a]	416 ± 82	767 ± 90 [a]
II	135 ± 26	556 ± 96 [b]	437 ± 86	807 ± 93 [a]
III	142 ± 14	588 ± 60 [b]	Total:391 ± 87	Total:720 ± 99 [a]
			Ph. A: 331 ± 76	Ph. A: 610 ± 89
			Ph. B: 60 ± 12	Ph. B: 110 ± 13

The means within a column followed by the same letter are not significantly different (α=0.05).

Table 3. Quality indexes for recovered oils from wet gums

Quality index	Method I	Method II	Method III
Acidity (g oleic acid kg^{-1})	16.9 ± 6.5 [a]	21.7 ± 7.3 [a]	16.7 ± 2.8 [a]
Peroxide value (mEq kg^{-1})	1.62 ± 0.49 [a]	1.02 ± 0.72 [a]	3.24 ± 1.98 [a]
p-Anisidine value	1.86 ± 1.50 [a]	4.03 ± 2.19 [a]	2.34 ± 0.76 [a]
Unsaponifiable matter (g kg^{-1})	9.0 ± 1.1 [a]	12.1 ± 2.0 [b]	11.5 ± 2.1 [a, b]
Phosphorous content (mg kg^{-1})	87 ± 34 [a]	330 ± 76 [b]	244 ± 73 [b]
TOTOX value [1]	5.09 ± 1.86 [a]	5.77 ± 2.42 [a]	8.82 ± 3.91 [a]

[1] Total oxidation value = 2 x peroxide value + p-anisidine value.

The means within a row followed by the same letter are not significantly different (α=0.05).

Table 4. Phospholipids composition for recovered oils (% relative)

Phospholipid	Method I	Method II	Method III
PE	17 ± 5 [a]	11 ± 6 [a]	12 ± 5 [a]
PA	7 ± 5 [a, b]	10 ± 4 [a]	5 ± 3 [b]
PI	14 ± 4 [a]	8 ± 2 [b]	6 ± 6 [b]
PC	62 ± 11 [a]	71 ± 10 [a]	77 ± 12 [a]
Total (g kg^{-1})	1.56 ± 0.64 [a]	9.56 ± 3.43 [b]	5.10 ± 4.16 [a, b]

The means within a row followed by the same letter are not significantly different (α=0.05).

Table 5. Polar compounds (g kg^{-1}) for recovered oils from wet gums

Compound	Method I	Method II	Method III
PTG	0.6 ± 0.1 [a]	0.5 ± 0.3 [a]	0.6 ± 0.1 [a]
DTG	0.0 ± 0.0 [a]	0.0 ± 0.0 [a]	0.0 ± 0.0 [a]
OTG	22.5 ± 3.6 [a]	21.2 ± 5.9 [a]	17.2 ± 2.1 [a]
DG	8.4 ± 3.8 [a]	6.8 ± 1.5 [a]	6.1 ± 1.3 [a]
FFA	24.6 ± 9.3 [a]	26.6 ± 7.9 [a]	24.9 ± 9.3 [a]
Total	56.1 ± 13.7 [a]	55.1 ± 10.7 [a]	48.8 ± 10.7 [a]
TD	23.1 ± 3.7 [a]	21.7 ± 6.1 [a]	17.8 ± 2.4 [a]
HD	33.0 ± 13.0 [a]	33.4 ± 9.4 [a]	31.0 ± 10.4 [a]
TD/HD	0.70 ± 0.24 [a]	0.65 ± 0.24 [a]	0.57 ± 0.16 [a]

PTG: Polymerized triglycerides, DTG: Dimerized triglycerides, OTG: Oxidized Triglycerides, DG: Diglycerides, FFA: Free fatty acids, TD: Thermal degradation=PTG + DTG + OTG, HD: Hydrolytic degradation=DG + FFA.

The means within a row followed by the same letter are not significantly different (α=0.05).

Table 6. Phospholipids composition for obtained lecithins

Phospholipid	Method I	Method II	Method III Phase A	Method III Phase B
PE				
(g kg^{-1})	185 ± 28 [a]	214 ± 21 [a]	218 ± 30 [a]	55 ± 10 [b]
(% Relative)	27 ± 3 [a]	31 ± 3 [b]	36 ± 2 [c]	33 ± 1 [b]
PA				
(g kg^{-1})	74 ± 5 [a]	94 ± 11 [b]	74 ± 14 [a]	22 ± 5 [c]
(% Relative)	11 ± 1 [a]	13 ± 2 [b]	12 ± 1 [a, b]	13 ± 1 [b]
PI				
(g kg^{-1})	113 ± 7 [a]	151 ± 5 [b]	107 ± 11 [a]	33 ± 6 [c]
(% Relative)	16 ± 1 [a]	22 ± 1 [b]	18 ±1 [c]	20 ± 2 [b, c]
PC				
(g kg^{-1})	319 ± 15 [a]	203 ± 4 [b]	211 ± 20 [b]	58 ± 12 [c]
(% Relative)	46 ± 2 [a]	29 ± 1 [b]	35 ± 1 [c]	35 ± 2 [c]
Total (g kg^{-1})	691 ± 53 [a]	662 ± 31 [a]	610 ± 70 [a]	168 ± 32 [b]

The means within a row followed by the same letter are not significantly different (α=0.05).