J. Korean Soc. Food Nutr.
20 (3), 220~224 (1991)

한국영양식량학회지

Effect of Degumming Reagents on the Recovery and Nature of Acetone Insolubles from Rice Bran Oil

Tae-Kyoo Lee†, Min-Whan Rho, Hee-Cheon Yang, Choong-Ki Kim*, Geun-Seoup Song*, Tai-Boong Uhm* and Yong-Ju Kwon*

Dept. of Food Science and Technology, Chonju Woosuk University, Wanju-kun 565-800, Korea
**Dept. of Food Science and Technology, Chobuk National University, Chonju 560-756, Korea*

Abstract

Six reagents (water, citric acid, phosphoric acid, oxalic acid, acetic anhydride and maleic anhydride) were evaluated for their effectiveness in degumming rice bran oil. All chemical reagents tested were found to be significantly more effective than water in removing phosphatides from crude rice bran oil. Especially acetic anhydride and phosphoric acid were effective in reducing phosphorous levels (92.5% and 93.3% removal, respectively). Nonhydratable phospholipids, lysophosphatidyl choline, were removed more effectively by the chemical reagents than by the water degumming. The major phospholipid(PL) components were phosphatidyl choline. Oleic, linoleic and palmitic acids were the major fatty acids of PL in rice bran acetone insolubles(AI). The AI recovered by acetic anhydride degumming produced the most stable emulsions. However, the AI obtained from phosphoric acid or oxalic acid treatments had very poor emulsifying properties.

Key words: rice bran oil, degumming reagents, lecithin, acetone insolubles

INTRODUCTION

Commercial lecithin is a complex of phosp-holipids (PL), glycolipids (GL), neutral lipids (NL) and non-PL compounds obtained during the refining of crude vegetable oils. Lecithin is used in foods primarily as emulsifer. Because the surface active properties of lecithin depend on its composition as well as physical structure, the degumming efficiency of various reagents could modify the PL composition to a point where emulsification properties are affected[1].

The PL compositions of soybean[2-6], sunflower[2], canola[2, 7], rapeseed[8] and rice bran lecithins[9] have been reported. Very few papers, however, have been published on the degumming reagents and conditions for rice bran oil[10] and on the changes in composition of rice bran lecithin depending on the degumming reagents.

The objectives of this study were to investigate the changes in the composition of rice bran acetone insolubles(AI) prepared with six degumming reagents and to compare the emulsification potentials of all prepared AI.

MATERIALS AND METHODS

Materials

Crude rice bran oil was obtained from Shinyang Rice bran Oil Co.. Phospholipid standards, phosphatidyl choline (PC), lysophosphatidyl choline (Ly PC), phosphatidyl ethanolamine (PE), phosphatidyl glycerol (PG), phosphatidic acid (PA) and phosphatidyl inositol (PI), were purchased from

† To whom all correspondence should be addressed

Sigma Chemical Co.(USA).

Degumming

Crude oil was heated to 60℃ with agitation of 200rpm. The levels and procedures for adding the degumming reagents were given by Diosady[7]. After the degumming, the oil was cooled to 40℃ and centrifuged 2,000rpm for 15min. The degummed oil was separated from the gummy lecithin residue by decantation.

Isolation of AI

AI were precipitated from the crude lecithin by the method of AOCS[11]. PL in the AI were separated by silicic acid column chromatography[12].

Composition of phospholipids

The isolated PL were separated into individual PL components on silica gel G TLC plates(200μm layer, Merck Co.) using chloroform-methanol-water (65 : 25 : 4, v/v/v). The components were identified by reaction with Dittmer and Lester spray reagents[13] and by comparing Rf values against standard samples.

The contents of individual PL were determined by using the TLC Scanner (Shiamdzu Model CS-900). The operational conditions were as following slit 1.25×1.25mm, wavelength 540nm and reflection by zig-zag mode.

Phosphorous analysis

Phosphorous in the crude and degummed oils were determined using the AOCS method[11].

Fatty acid composition

The fatty acids were rapidly methylated by using BF_3 methanol solution[14].

A gas chromatograph (PYE UNICAM model 4500) equipped with a six-ft glass column(4mm I.D.× 2m) packed with GP 10% SP-2330 on chromosorb WAW(100-120mesh) was used for fatty acid analysis. The oven temperature was maintained at 200℃ and the injection port and detector temperatures were 250℃. The flow rate of nitrogen carrier gas was 50ml/min. Peak area was calculated with an integrator without consideration of FID response factors.

Emulsification

Oil and water emulsions were prepared by dispersing 0.05% AI in 60ml soybean oil with constant stirring and heating. Forty ml of water was added to this mixture and the emulsion was prepared by homogenizing for 5 min at 10,000 rpm. After the emulsions wer stood for 60 hours in room temperature, phase separation was measured using mess cylinder to obtain a relative assessment of the emulsion stability.

RESULTS AND DISCUSSION

Degumming effectiveness

The efficiency of degumming was evaluated directly by comparing residue phosphorous (P) in the degummed oils. The results show that all chemical reagents used in this study were significantly more effective than water in removing from the crude rice bran oil (Table 1).

Table 1. Degumming effectiveness of various degumming reagent

Degumming reagent	Reagent added (g/kg oil)	ppm P in degummed oil
Acetic anhydride	2.5	50
Maleic anhydride	2.5	55
Phosphoric acid	1.7	45
Oxalic acid	2.0	75
Citric acid	2.5	60
Water	—	120
Crude oil	—	670

According to Smiles et al[2]. an effective degumming reagent showed reduced P content in degummed vegetable oils to below 50 ppm. In our experiment phosphoric acid and acetic acid treated rice bran oil contained 45 and 50 ppm of phosphorous, respectively. Accordingly, phosphoric acid and acetic anhydride succeeded in producing acceptable P levels in crude rice bran oil. Based on the total P content of the crude undegummed oils and the subsequent reduction of P with water degumming, rice bran oils were shown to contain about 18% nonhydratable PL (NHPL).

Quantitative TLC analysis of PL in AI

The TLC chromatograms of PL in rice bran AI are shown in Fig. 1, and the relative compositions of individual PL in AI are shown in Table 2.

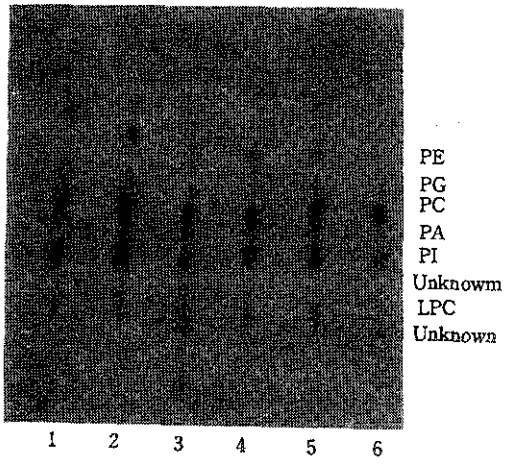

Fig. 1. TLC chromatogram of phospholipids in acetone insolubles degummed by various reagents. 1 : acetic anhydride, 2 : citric acid, 3 : maleic anhydride, 4 : oxalic acid, 5 : phosphoric acid, 6 : water, PE : phosphatidyl ethanolamine, PG : phosphatidyl glycerol, PC : phosphatidyl choline, PA : phosphatidic acid, PI : phosphatidyl inositol, LPC : lysophosphatidyl choline. Solvent system : chloroform-methanol-water(65 : 25 : 4, v/v/v)

Table 2. Relative phospholipid composition of acetone insolubles

Degumming reagent	Phospholipid (%)						
	PE	PG	PC	PA	PI	LPC	UK
Acetic anhydride	10.2	3.9	51.1	4.3	17.7	10.3	2.5
Citric acid	14.4	3.1	50.2	4.0	17.3	9.0	2.0
Maleic anhydride	10.2	1.3	48.5	3.1	15.6	11.4	6.9
Oxalic acid	14.0	2.6	48.1	3.4	19.8	10.0	2.1
Phosphoric acid	12.5	3.7	49.1	3.6	14.2	15.9	1.0
Water	11.1	4.5	50.4	3.9	15.2	5.5	9.4

PE : phosphatidyl ethanolamine, PG : phosphatidyl glycerol, PC : phosphatidyl choline, PA: phosphatidic acid, PI: phosphatidyl inositol, LPC : lysophosphatidyl choline, UK : unknowns.

The results indicated that the chemical degumming reagents did not greatly alter the PL profiles. Phosphoric acid has been known for its ability to promote hydration of those PL consid-ered to be nonhydratable (Lyso PC and PA). Also citric acid was found to be significantly better than water in removing PA from soybean and sunflower oils[2].

In the case of hydratable PL, all chemicals were shown to be similar in PC removal. Oxalic acid was the most effective among the treated reagents in extracting PI and citric acid in extracting PE.

These results showed that although the PL were removed to a greater extent when using chemical degumming reagents than with water (Table 1), the relative compositions of the individual PL components were not substantially changed.

When the PL compositions of rice bran AI were compared to other oil seed AI using the results from water degumming, PC content in rice bran AI (48-51%) was higher than those in soybean AI, canola AI and sunflower AI (about 33-35%). This result may be come from the fact that the band identified as PC on TLC chromatogram was not a sole band but a mixture band of PC and phosphatidyl serine (PS). The fact that PS was contained in PL of rice bran oil was also found in the report by Ryu and Cheigh[15].

Fatty acid composition

The different degumming reagents did not affect greatly the fatty acid composition of PL, but some minor variations were noted (Table 3).

Table 3. Fatty acid composition of phospholipids in acetone insolubles

Degumming reagent	Fatty acid (%)				
	16 : 0	18 : 0	18 : 1	18 : 2	18 : 3
Acetic anhydride	19.0	1.8	44.1	34.4	0.7
Citric acid	22.7	1.4	42.8	32.6	0.5
Maleic anhydride	21.3	1.5	43.5	33.0	0.7
Oxalic acid	24.4	2.0	41.6	31.5	0.5
Phosphoric acid	23.4	1.7	44.1	30.4	0.4
Water	20.4	1.3	43.1	34.3	0.4

The major fatty acids of PL in rice bran AI were oleic, linoleic and palmitic acid in decreasing order, regardless of the kinds of degumming reagents. When the fatty acid profile of PL from rice bran AI was compared with to those of other vegetable oils, unsaturated fatty acid content was similar to those of PL from soybean and sunflower AI (77-78%), and the fatty acid profiles were similar to that of PL from canola AI (oleic acid 46.2%, linoleic acid 36.1% and palmitic acid 11.3%)[2].

Emulsification properties of AI

Emulsion stabilizing ability of rice bran acetone insolubles degummed various reagents are shown

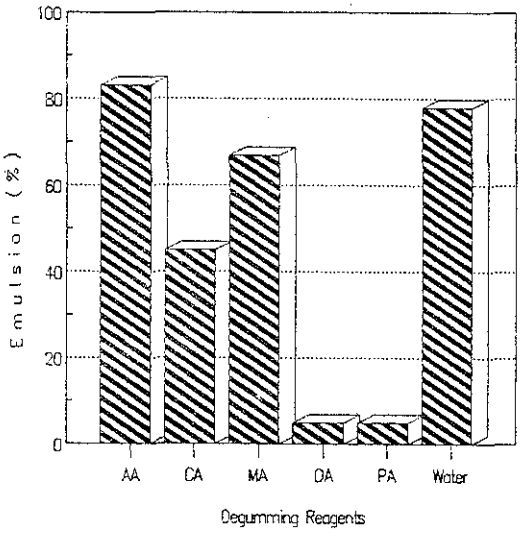

Fig. 2. Emulsion(60 : 40, oil/water) stabilizing ability of rice bran acetone insolubles degummed by various reagents. AA : acetic anhydride, CA : citric acid, MA : maleic anhydride, OA : oxalic acid, PA : phosphoric acid

in Fig. 2. The results show that AI obtained from acetic anhydride produced the most stable emulsions. Water, citric acid and maleic anhydride-extracted AI produced emulsions with similar stability, whereas the emulsifying properties of oxalic and phosphoric acid-treated AI were generally poor, even though their PL compositions were similar to those other chemicals-treated AI.

Smiles et al[1]. reported that charged anionic PL (i. e. PI and PA) are responsible for improving the emulsification properties of the lecithin mixture. This study, however, showed that the level of PI in phosphoric acid-extracted AI was lower than that found in water-degummed AI, while the level of PI in oxalic acidtreated AI was significantly higher than that found in water degummed AI. The levels of PA in all the degumming reagents-extracted AI were not significantly different from one another. The results of poor emulsion stabilities of oxalic and phosphoric acid-treated AI were in good agreement with the report of Smiles et al[1]. They thought that traces of phosphoric and oxalic acids were not completely removed by twice acetone washings.

Therefore this study indicated that although the PL composition of AI did not vary dramatically, emulsion stability was affected by the various degumming reagents. Apart from the AI extracted with water degumming, those AI recovered with citric acid and anhydride reagents showed potential as food grade emulsifying agents.

REFERENCES

1. Smiles, A., Kakuda, Y. and MacDonald, B. E. : Effect of degumming reagent on the composition and emulsifying properties of canola, soybean, and sunflower acetone insolubles. *JAOCS*, **66**, 348 (1989)
2. Smiles, A., Kakuda, Y. and MacDonald, B. E. : Effect of degumming reagent on the recovery and nature of lecithins from crude canola, soybean, and sunflower oils. *JAOCS*, **65**, 1151 (1989)
3. List, G. R., Avellaneda, J. M. and Mounts, T. L. : Effect of degumming condition on removal and quality of soybean lecithin. *JAOCS*, **58**, 892 (1981)
4. Racicot, L. K. and Handel, A. P. : Degumming of soybean oil quantitative analysis of phopholipids in crude and degummed oil. *JAOCS*, **60**, 1098 (1983)
5. Schofield, C. R. : Composition of soybean lecithin. *JAOCS*, **58**, 889 (1981)
6. Weber, E. J. : Composition of commercial corn and soybean lecithins. *JAOCS*, **58**, 898 (1981)
7. Diosady, L. L. : Chemical degumming of canola oils. *JAOCS*, **59**, 313 (1982)
8. Persmark, U. : *Rapseed cultivation composition processing and utilization*. Appelgvist, L. A. and Ohlson, R. (eds.), Elsevier Publishing Co., New York, p. 288 (1972)
9. Adhikari, S. and Adhikari, J. : Indian rice bran lecithin. *JAOCS*, **63**, 367 (1986)
10. Kim, S. K., Yoo, S. H., Kim, C. J. and Cheigh, H. S. : Effect of oxalic and phosphoric acid on degumming of rice bran oil. *J. Korean Food Sci. Technol.*, **17**, 128(1985)
11. A.O.C.S. : *Official and tentative method*. Vol 1 and 2. 3rd and revised edition (1977)
12. Rouser, G., Kritchevsky, G., Simon, G. and Nelson, G. J. : The separation of complex lipid mixtures by the use of silicic acid chromatography. *Lipids*, **2**, 37 (1967)
13. 藤野安山 : 脂質分析法 入門. 學會出版, 東京(1980)
14. Firestone, D. and Horwitz, W. : IUPAC gas chromatography method for determination of fatty acid composition. *J. Assoc. Off. Anal. Chem.*, **92**, 709 (1979)
15. Ryu, C. H. and Cheigh, H. S. : Fractionation of rice bran lipid and storage effect on rice bran lipid composition. *J. Korean Food Sci. Technol.*, **12**, 278 (1980)

(Received January 17, 1991)

미강유로부터 Acetone Insolubles 회수 및 성질에 미치는 탈검제의 영향

이태규, 노민환, 양희천, 김충기*, 송근섭*, 엄태붕*, 권용주*

전주우석대학교 식품공학과
*전북대학교 식품공학과

요 약

물 및 다섯가지 탈검제(citric acid, phosphoric acid, oxalic acid, acetic anhydride 및 maleic anhydride)를 사용하여 미강유를 탈검하고 그 탈검효율을 비교하였다. 미강유 원유로부터 인 함유 물질을 제거하는데 있어서 모든 탈검제가 보다 효과적이었으며, 특히 acetic anhydride와 phosphoric acid는 각각 92.5% 및 93.3%까지 인 함유율을 저하시켰다. 또한 비수화성 인지질 특히 Lyso PC를 제거하는데 있어서 모든 탈검제가 효과적이었다. 미강유로부터 추출한 AI의 인지질은 주로 PC, PI, PE 및 Lyso PC로 구성되어 있었으며, 주요 지방산은 oleic acid, linoleic acid 및 palmitic acid의 순이었다. Acetic anhydride를 사용하여 얻은 AI가 가장 안정된 유화를 형성하였으며, 반면에 phosphoric acid 및 oxalic acid를 처리하여 얻은 AI는 매우 빈약한 유화성을 나타냈다.