Oxidative Stability of High-Fatty Acid Rice Bran Oil at Different Stages of Refining

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The contents of natural antioxidants and the oxidative stability of rice bran oils at different refining steps were determined. Tocopherols and oryzanols were constant in crude and degummed oils but decreased in alkali-refined, bleached and deodorized oils. The process of degumming, alkali-refining, bleaching and deodorization removed 34% of the tocopherols and 51% of the oryzanols. During storage of deodorized oil for 7 wk, 34% of the tocopherols and 19% of the oryzanols were lost. The maximum weight gain, peroxide value and anisidine value were obtained from alkali-refined oil during storage. The order of oxidation stability was crude ≥ degummed > bleached ≒ deodorized > alkali-refined oil.

KEY WORDS: Anisidine value, oryzanols, oxidative stability, peroxide value, refining, rice bran, tocopherols, weight gain.

Rice bran oil is generally obtained by solvent extraction and processed by degumming, alkali-refining, bleaching, winterizing and deodorizing to obtain bland and clear salad oil (1). Although refining removes objectionable impurities, it also removes advantageous materials, such as natural antioxidants, synergists and biologically active materials (2).

Rice bran is susceptible to deterioration after polishing because of high lipase activity (3). Crude rice bran oil, however, possesses excellent oxidative stability because it contains considerable amounts of tocopherols and oryzanols (4).

Several papers have reported the oxidation and stability of vegetable oils during processing. Going (5) reported that refined and bleached soybean oil was more easily oxidized than crude oil according to peroxide value determination, Kwon *et al.* (6) reported that crude soybean oil was most stable among degummed, refined, bleached and deodorized oils based on weight gain during storage. Jung *et al.* (7) reported that crude soybean oil was stable during storage while refined and bleached oil was unstable by comparison of molecular oxygen disappearance in the headspace of oil samples.

The objectives of this paper were to examine the effects of refining steps on the contents of tocopherols and oryzanols, and on the oxidative stability of rice bran oil at different refining stages.

MATERIALS AND METHODS

Materials. Fresh, crude rice bran oil was obtained from a commercial refinery. Degumming, alkali-refining, bleaching and deodorizing processes were substantially the same as described in Kim *et al.* (8). Crude oil was degummed by 4% oxalic acid (20 mL/kg oil) at 60°C with slow agitation for 20 min. Degummed oil was deacidified by 24 Baume KOH solution (0.5% excess) at 70°C with mild stirring for 15 min. Refined oil was bleached by 12% activated clay at 105°C with vigorous stirring for 20 min under 1 mm Hg vacuum. Bleached oil was deodorized by steam distillation with 2% steam at 235°C for 1 h under 3 mm Hg vacuum. All reagents were of analytical grade unless otherwise specified.

Analytical methods. Phosphorus, acid value and peroxide value were determined by AOCS methods Ca 12-55, Cd 3a-63 and Cd 8-53, respectively (9). Anisidine value and total sterols were determined by IUPAC methods 2.504 and 2.404, respectively (10). Tocopherols were determined by high-performance liquid chromatography (HPLC) (11), and oryzanols were determined spectrophotometically at 315 nm (12).

Sample preparation for oil oxidation and its determination. Fifteen-gram oil samples in open glass petri dishes (i.d. 10 cm) were stored at 50°C for 2 to 7 mon in a dark oven. Oxidative stability of oil was measured by a combination of weight gain, peroxide value and anisidine value. Weight gain, expressed as the increase of weight (mg)/g of oil, was measured according to the method of Olcott and Einset (13).

Statistical analysis. The analytical data of the effects of refining steps on the weight gain, peroxide value, anisidine value, tocopherol contents and oryzanol contents in rice bran oil were analyzed by Duncan's Multiple Range Test (14).

RESULTS AND DISCUSSION

Effects of processing steps on the contents of minor compounds in rice bran oil. Oil processing by degumming, alkali-refining, bleaching and deodorizing removed phosphorus almost completely, 98.7% free fatty acids, 34% tocopherols, 51% oryzanols and 5% sterols. Crude oil contained 677 ppm phosphorus, which was equivalent to 2% phospholipids (conversion factor = 30). Degumming removed 98.5% of phospholipids in crude oil, and alkali-refining removed 90% of phospholipids from degummed oil. Phosphorus was not detected in bleached and deodorized oils. The complete refining process removed 98.7% of free fatty acids in crude oil. Degumming increased acid value from 23.7 of crude oil to 26.5 while refining decreased it from 26.5 to 0.4. Bleaching increased it from 0.4 to 0.6. This was due to hydrolysis of triglycerides by water present in oxalic acid and activated clay at higher temperature (15). Deodorization removed 50% free fatty acids from bleached oil. Refining and deodorizing appeared the most important steps to reduce free fatty acids, and, therefore, to control the acid value in rice bran oil. Peroxide compounds were not detected in deodorized oil. The anisidine value decreased from 63.4 to 40.1 after whole refining. Ninty-five percent of the sterols was contained in deodorized oil, whereas only 66% tocopherols and 49% oryzanols were retained. Oryzanols, ferulic acids esterified with alcohols, sterols and/or triterpenoids were uniquely found in rice bran oil at a total level of 18,560 ppm. The high oxidative stability of crude rice bran oil is due to the antioxidant activity of oryzanols (4). Alkali-refining removed 47% oryzanols from crude oil.

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TABLE 1

Duncan's Multiple Range Test for the Effects of Refining Steps on the Weight Gain, Peroxide Value, Anisidine Value, Tocopherol Contents and Oryzanol Contents in Rice Bran Oil During Ten Weeks of Storage at 50°C[a]

Oil sample	Weight gain (mg/g)	Peroxide value	Anisidine value	Tocopherols (ppm)	Oryzanols (%)
Crude	0.7 B	5.7 B	66.2 B	6529 A	1.61 A
Degummed	1.3 B	18.4 B	72.1 B	6719 A	1.64 A
Refined	11.9 A	367.1 A	134.7 A	3504 C	0.77 C
Bleached	7.6 AB	296.5 A	54.6 B	4329 B	0.87 B
Deodorized	7.2 AB	316.7 A	57.3 B	4475 B	0.88 B

[a]Values with the same letter are not significantly different at $\alpha = 0.05$ (Duncan's tests were carried out for weight gain, peroxide value, anisidine value, tocopherols and oryzanols, independently).

Oxidative stability of rice bran oils at different refining steps. Oxidative stability of oil samples during storage were determined by weight gain, peroxide value and anisidine value. Results obtained from Duncan's Multiple Range Test for the effects of refining steps on weight gain, peroxide value, anisidine value, tocopherol contents and oryzanol contents in rice bran oil are shown in Table 1. The schematic illustration of the changes of analytical values is given in Figure 1.

Weight of alkali-refined oil increased gradually during the first five weeks of storage and increased sharply thereafter. Weight gain of alkali-refined oil was the highest, followed by those of bleached and deodorized oils, and that of crude oil was the lowest at the significance level of $\alpha = 0.05$ (Table 1). Oils with higher rates of weight increase possess lower oxidation stability (6,13). Crude oil was the most stable to oxidation. Oxidative stabilities of bleached and deodorized oils were similar, whereas alkali-refined oil was the least stable among those tested. The order of oxidation stability, determined by weight gain, was crude ≒ degummed, bleached ≒ deodorized, and alkali-refined oil. This trend was also shown in the changes of peroxide values. By the determination of peroxide value, crude oil was most stable, and degummed, bleached and deodorized, and alkali-refined oil were less stable in decreasing order. Anisidine values of bleached and deodorized oils increased quite similarly following refined oil. The order of oxidative stability determined by anisidine value was crude, degummed, bleached ≒ deodorized and refined oil. Based upon the results of weight gain, peroxide value and anisidine value, it was shown that crude oil was the most stable, and degummed oil was less stable than crude oil. Oxidative stabilities of bleached oil and deodorized oil were about the same but were less stable than degummed oil. Alkali-refined oil was the least stable among oils tested. Kwon *et al.* (6) reported that the order of oxidative stability of different soybean oils was crude, degummed, bleached, deodorized and refined oils by determination of weight gain. The differences of oxidative stability among bleached, deodorized and refined oils, however, were not large. They reported that the more refined the soybean oil was, the lower the stability because natural antioxidants were eliminated from the oil. Jung *et al.* (7) reported crude soybean oil was most stable, and deodorized, degummed, refined and bleached oil were less stable in decreasing order by the determination of molecular oxygen contents in the headspace. They reported that this was due to the loss of natural antioxidants and synergists, such as tocopherols and phosholipids (16,17). However, they showed that deodorization increased oxidative stability of soybean oil because prooxidants remaining in the bleached oil, such as moisture, monoglycerides and free fatty acids, were removed during deodorization (18,19).

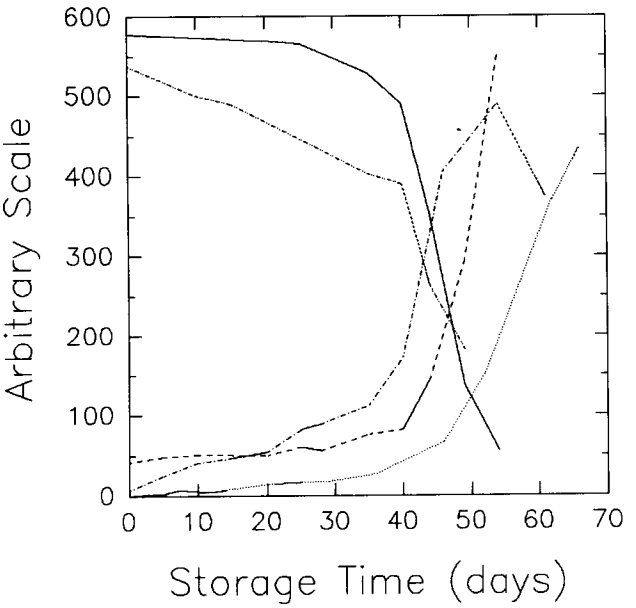

FIG. 1. Changes of weight gain and minor compound contents in alkali-refined rice bran oil during storage. ·····, Weight gain; ——, anisidine value; –·–·–, peroxide value; –· –· –·, tocopherol content; — —, oryzanol content.

Tocopherol contents of different soybean oils changed during storage (Fig. 1). Crude and degummed oils contained quite constant levels of tocopherols, ranging from 7,150 to 6,030 ppm, during ten weeks' storage. Tocopherol contents in bleached and deodorized oils, however, decreased gradually as storage proceeded. Tocopherols in refined oil decreased slowly until 38 d of storage and decreased sharply thereafter; they reached 1,830 ppm after seven weeks' storage. Tocopherols are oxidized in air and decomposed into several decomposition products (20,21). Initial contents of oryzanols in crude and degummed oils

were 1.58 to 1.71%, respectively, and remained almost constant during ten weeks' storage (Fig. 1). After alkali-refining, oryzanol content decreased to 9,770 ppm. Oryzanols in refined and bleached oils decreased gradually during storage. In refined oil, oryzanol content decreased slowly until 38 d and decreased rapidly thereafter. Oryzanols and tocopherols decomposed simultaneously as noted previously (22). The excellent oxidative stability of rice bran oil is due to intrinsic tocopherols and oryzanols (4,23). Tocopherols and oryzanols decreased sharply after five weeks' storage, and weight gain, peroxide value and anisidine value of alkali-refined oil increased sharply.

Crude rice bran oil is the most advantageous for storage to avoid oxidation, and storage of alkali-refined, bleached and/or deodorized rice bran oil is not beneficial because of low oxidation stability and large refining losses.

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