Retarding Autoxidation in Raw Peanut Oil by Addition of Water

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ABSTRACT: Addition of water at levels of 0.25 to 1.00% (wt/vol) to raw peanut oil inhibited the formation of peroxides in the oil. The free fatty acid content of oils to which water had been added also did not increase appreciably compared to a control oil. To improve the stability of the oil, a moisture content of 0.2%, which is about ten times higher than the Brunauer-Emmett-Teller monomolecular moisture content of the oil, has been suggested.

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KEY WORDS: Antioxidant, peanut oil, relative humidity, water, water activity.

We reported earlier (1,2) that the rate of peroxide development in expeller-pressed peanut oil (PNO) decreased with relative humidity (RH = aw × 100), whereas in degummed oil the rate increased with RH (aw) values. However, the free fatty acid content of the oil remained similar during storage at different RH (aw) values. Subsequently, it was found that native gums acted as powerful antioxidants when they were humidified to 91% RH (aw = 0.91) (3). Generally, equilibrating the oil to a high humidity is a cumbersome and time-consuming process from the commercial application point of view. Therefore, instead of humidification of the oil to 91% RH (aw = 0.91), addition of the required quantity of water to raw PNO has been attempted for commercial application, the results of which are given in this paper.

MATERIALS AND METHODS

Materials. Expeller-pressed PNO (raw PNO) was purchased from the local market. Its chemical characteristics are reported in Table 1, and the procedures used for the determination of color (1), density (1), viscosity (4), iodine value (1), free fatty acids (1), peroxide value (1), phospholipids content (1), fatty acid composition (1), total tocopherols (3), iron and copper contents (3), moisture content (5), and sensory property evaluation (1) have been described previously.

To determine the equilibrium moisture content (EMC) of raw PNO stored at different RH (aw), the oil samples were placed (in duplicate) in desiccators maintained at 22, 50, 67, and 91% RH (0.22, 0.50, 0.67, and 0.91 aw, respectively) by using saturated salt solutions (6), and the samples were weighed once each 24 h until they attained constant weight (within ten days all samples were equilibrated). The percent increase in weight of a sample was calculated by using the formula: (equilibrated oil weight − initial dry weight) × 100/dry weight of the sample, which is the EMC of the oil. From this EMC value, the Brunauer-Emmett-Teller (BET) monomolecular moisture content was calculated graphically by following the methods described by Wink (7) and Salwin (8).

TABLE 1
Chemical Characteristics of Raw Peanut Oil

Parameter	Unit of measurement	Value
Lovibond color	5R + Y units	5.0
Density	mL	0.9145
Viscosity	milli Poise	418
Iodine value (Wijs)	g Iodine absorbed/100 g oil	100.0
Free fatty acids	as % oleic	0.9
Peroxide value	meq O_2/kg oil	1.2
Phospholipids content	g%	0.2
Total tocopherols	mg%	25.0
Iron	ppm	<0.05
Copper	ppm	<0.05
Fatty acid composition	relative %	
$C_{16:0}$		17.0
$C_{18:0}$		1.8
$C_{18:1}$		46.0
$C_{18:2}$		30.8
$C_{20:0}$		3.1
$C_{24:0}$		1.3

To study the effect of added water on autoxidation of the oil, raw PNO was dried over fused calcium chloride under vacuum for 24 h at 27°C. The dried oil (100 mL) was placed in 250-mL Erlenmeyer flasks. Distilled water at different levels (0.00, 0.25, 0.50, 0.75, and 1.00 g, five treatments in duplicate) was added to the oil and mixed well on a magnetic stirrer for 10 min. Then the flasks were stoppered and stored in an incubator (in the dark) at 40°C. Periodically, the samples were withdrawn for peroxide value determination (9).

RESULTS AND DISCUSSION

The raw PNO stored at 22 and 50% RH did not pick up any moisture but lost 0.09 and 0.04% moisture, respectively. The initial moisture content of the oil was 0.09%, and at 67 and

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91% RH it picked up 0.06 and 0.16%, respectively. This indicated that only at 91% RH there was a substantial pick up of moisture. Therefore, incorporation of water directly into the oil to the extent of 0.25% (the desired level) was tried instead of equilibrating the oil to 91% RH.

Effect of added water to raw PNO on peroxide development. The EMC of the oil stored over 91% RH was found to be 0.25% (0.247 ± 0.010%). This was 11.5 times the estimated BET monomolecular moisture value of 0.022%. Yet, contrary to the known behavior of model lipid systems (10,11) and refined vegetable oils (3,12), the raw oil in the present study, as well as in earlier studies (1), oxidized slowly at 91% RH. The refined PNO and degummed raw PNO did not pick up any moisture when stored over 91% RH (0.91 aw) (Verma, M.M., and J.V. Prabhakar, unpublished data). Therefore, it was inferred that the constituents of gums (mainly phospholipids), which can take up 23 moles of water per gram of the lipid (13), were mainly responsible for the high EMC of the oil. The expeller-pressed oil had a total phospholipids content of 0.2%. This means that the phospholipids in the oil alone could take up 0.11 g of water per 100 g oil theoretically (assuming phosphatidylcholine as the phospholipid). The results of the present study show that phospholipids in their natural state in raw oil may have taken up more moisture than expected. The reason for this is not known. However, it may be argued that the hydration behavior and antioxidant property of purified phospholipids might be different from their behavior in the natural state when present in the oil. Differences in the antioxidant activity of purified phospholipids and the phospholipids in their natural state in the oil have been observed before (3).

While equilibration of the expeller-pressed oil to 91% RH (0.91 aw) (EMC = 0.25%) was effective in retarding autoxidation, higher levels of added water from 0.25% up to 1.0% in the oil did not exhibit increases in peroxide values with increasing storage periods over a period of 15 wk (Table 2).

TABLE 2
Effect of Addition of Water on Autoxidation Stability of Raw Peanut Oil

	Storage period (wk)							
	0		5		10		15	
Sample	PV[a]	FFA[b]	PV	FFA	PV	FFA	PV	FFA
1. Raw peanut oil (moisture-free)	1.2	0.70	10.0	0.70	29.0	0.75	49.0	0.85
2. Oil 1 + 0.25% water	1.2	0.74	1.2	0.78	1.2	0.81	1.2	0.85
3. Oil 1 + 0.50% water	1.2	0.73	1.2	0.76	1.2	0.81	1.2	0.85
4. Oil 1 + 0.75% water	1.2	0.74	1.2	0.78	1.2	0.80	1.2	0.85
5. Oil 1 + 1.00% water	1.2	0.74	1.2	0.78	1.2	0.83	1.2	0.86

[a]PV = Peroxide value expressed as milli equiv. O_2/kg oil.
[b]FFA = Free fatty acids (as % oleic).

TABLE 3
Effect of Addition of Water on Smell and Appearance of Raw Peanut Oil

	Smell of the oil		Appearance after 15 wk
Sample[a]	after 0 wk	after 15 wk	(visual)
1	Fresh	Rancid	Clear
2	Fresh	Fresh with a slight boiled-milk smell	Hazy
3	Fresh	Objectionable smell	Cloudy
4	Fresh	Objectionable smell	Cloudy
5	Fresh	Objectionable smell	Cloudy

[a]Same as in Table 2.

However, only the sample treated with 0.25% moisture had a slight aroma, similar to boiled milk, and a little cloudy appearance (comparable to fresh raw oil). The remaining samples with 0.50, 0.75, and 1.0% water treatment had an unacceptable and objectionable smell (Table 3), although the peroxide values were similar to 0.25% water-treated oil (Table 2). The control oil (moisture-free oil) was distinctly rancid by the end of 15 wk and had a 40-fold increase in peroxides but similar free fatty acid content. Hence, the study indicated that addition of water from 0.15% [EMC at 67% RH (0.67 aw)] up to 0.25% [EMC at 91% RH, (0.91 aw)] reduced the rate of autoxidation in the oil. Therefore, raw PNO is expected to have maximum storage stability at about 0.20 ± 0.05% water content. Based on this study, it is suggested that expeller-pressed PNO with 0.2% moisture could have a better shelf-life compared to a completely dry oil (moisture-free oil).

The list of permitted synthetic antioxidants is shrinking day by day due to their suspected health hazards and the growing desire of the public to use only natural substances in foods. The use of natural substances, such as water and phospholipids, therefore, is believed to bring a new dimension to the field of natural antioxidants applications in foods.

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