Antioxidant Efficacy of Water Washed Gums as a Function of Relative Humidity in Peanut Oil

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ABSTRACT

The stability of raw peanut oil to autoxidation at 40 C increased with ambient relative humidity, reaching a maximum stability at 90.5% RH ($K_M \times 10^{-3}$ 2.54, 1.83, 0.50 meq O_2/kg/hr at RH of 2, 47.5, 90.5%, respectively). Degumming with water or with phosphoric acid accelerated autoxidation at all test humidities. The trend in the rate of autoxidation was opposite that of the raw oil, increasing with relative humidity. It reached its maximum at 90.5% RH ($K_M \times 10^{-3}$ of 3.93, 3.16, 6.65 meq O_2/kg/hr at RH of 2, 47.5, 90.5% respectively for phosphoric acid degummed oil). Adding back the water washed gums removed during degumming to the water degummed peanut oil substantially restored the stability of the oil to autoxidation. These studies indicate that water washed gums retain most of their native state antioxidant activity. Hence, the gums removed during processing of oils could be added back to the oil after final processing to impart increased stability to the oil in some applications. The antioxidant efficacy of water washed gums was as good as that of synthetic antioxidants. These have an advantage over synthetic antioxidants in that they are natural components of most oils and fats.

INTRODUCTION

In an earlier communication from this laboratory, we reported that expeller pressed peanut oil was comparatively more stable to autoxidation at high relative humidities (RHs) than at low RHs (1). Native phosphatides and gums in the unrefined peanut oil were suspected to be the factors responsible for this observation. In this paper, effects of degumming and addition of water washed gums on the stabilities of peanut oils at different relative humidities are reported.

EXPERIMENTAL PROCEDURES

Materials

Unrefined and alkali refined (undeodorized) peanut oils were procured from the local market. Propyl gallate (PG) and butylated hydroxy toluene (BHT) used were food grade antioxidants and DL-α-tocopherol (α-T) was purchased from M/s E. Merck, Darmstadt, West Germany. Unrefined peanut oil (hereafter referred to as raw oil) was divided into three portions. One portion without any treatment served as control. The second portion was degummed at ambient temperature using two parts of distilled water to 100 parts of oil (w/w). The gums were separated by centrifugation and freeze dried. The gums so prepared, hereafter referred to as water washed gums, had the following composition: neutral lipids (85%), glycolipids (10%) and phospholipids (5%). The third portion was degummed at 55 C using distilled water (2 parts) and phosphoric acid (0.2 parts) to 100 parts of oil (w/w/w). After separation of the gums by centrifugation, the oil was washed repeatedly with distilled water until free from phosphoric acid. The analyses of the raw, degummed and alkali refined oils are given in Table I.

Oil samples (100 ml) were placed in 250 ml Erlenmeyer flasks. A 10 ml beaker containing 5 ml saturated salt solution (6 g of fused calcium chloride lumps were used for 2% RH) was suspended inside the flask using a thread tied to the stopper as shown in Figure 1 to obtain the desired RH (2). The flask was sealed with the stopper, and the oil was stirred for 5 min using a magnetic stirrer. The assembled flasks were left in an incubator maintained at 40±1 C. Before and after periodic withdrawals of sample for analysis the oil in the flask was stirred for 3 min as described above.

To degummed peanut oil, freeze dried peanut oil water washed gums were added back (approximating the amounts removed during degumming), and the oil was mixed thoroughly using a magnetic stirrer.

To refined peanut oil 200 ppm of propyl gallate or BHT or α-tocopherol was added, and the oil was mixed thoroughly using a magnetic stirrer.

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TABLE I

Characteristics of Raw, Degummed and Refined Peanut Oils

Analysis	Raw peanut oil	Peanut oil degummed using		Refined peanut oil
		Water	Phosphoric acid	
Phospholipids (%)	0.50	0.1	0.06	0.10
Free fatty acids (as % oleic acid)	0.86	0.6	0.58	0.20
Peroxide value (meq O_2/kg)	2.00	2.0	8.3	10.1

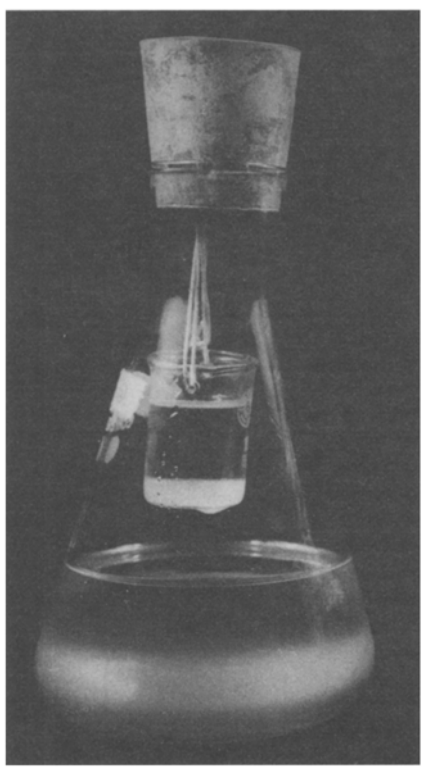

FIG. 1. The reaction flask used for the autoxidation studies at a known relative humidity. The beaker suspended from the cork contains the saturated salt solution of known humidity, and the autoxidizing oil is in the flask.

TABLE II

Effects of Degumming Methods on the Oxidative Stability of Peanut Oil Stored at Different Relative Humidities (RH)[a]

Storage period (weeks)	Peroxide value (meq O_2 /kg)													
	Raw peanut oil at RH (%)					Phosphoric acid degummed peanut oil at RH (%)					Water degummed peanut oil at RH (%)		Water degummed peanut oil + peanut oil water washed gums at RH (%)	
	2	20	47.5	67	90.5	2	20	47.5	67	90.5	2	90.5	2	90.5
1	4.2	2.2	2.2	2.2	2.2	13.2	13.2	17.9	20.2	20.2	8.9	6.1	5.7	4.4
2	4.4	2.2	4.4	2.1	2.0	15.0	17.9	21.0	25.4	29.0	14.9	10.3	10.4	5.9
4	6.6	6.5	4.4	4.3	2.2	19.6	19.8	29.1	33.2	41.8	30.7	16.3	24.4	9.4
6	13.7	14.1	8.2	5.2	2.5	31.7	25.4	32.0	45.6	61.6	–	–	–	–
9	–	–	–	–	–	–	–	–	–	–	65.7	33.7	57.9	21.6
10	33.0	34.0	19.8	12.8	4.3	72.1	50.8	65.8	92.1	202.3	–	–	–	–
$K_M \times 10^{-3}$ (meq O_2 / kg/hr)	2.54	2.63	1.83	1.32	0.50	3.93	2.63	3.16	4.05	6.65	5.42	2.98	4.12	2.05

[a]The initial peroxide values of raw, water degummed and phosphoric acid degummed peanut oils were 2.0, 2.0 and 8.3 meq O_2 /kg oil, respectively.

Analytical Methods

Peroxide and free fatty acid values and phospholipid content were estimated according to the procedures described earlier (1). Glycolipids were estimated according to the procedure of Dubois et al. (3) after fractionation of water washed gums into neutral, glyco- and phospholipids on silicic acid column (4). Oxygen uptake was measured using manometric technique (5) taking 2.5 ml of peanut oil in the main vessel and 0.5 ml of different saturated salt solutions (0.75 g of fused calcium chloride for 2% RH) in the side arm of 25 ml precalibrated Warburg flasks. This procedure was convenient for maintaining the RH at the desired level. Oxygen uptake by the samples was measured at 37±0.1 C.

RESULTS AND DISCUSSION

The changes in peroxide value of raw and degummed peanut oils during storage at different RH's are given in Table II. Peroxide value in raw peanut oil increased rather slowly at all RH's; at 90.5% RH it was extremely slow. However, in peanut oil degummed with phosphoric acid, there was a noticeable increase in peroxide value at all RH's within one week of storage. On further storage of the degummed oil, the peroxide value increased with RH and recorded a value as high as 200 meq O_2/kg at 90.5% RH after 10 weeks of storage. When the oil was degummed with only water, the rate of peroxide formation at 90.5% RH was considerably lower than that of phosphoric acid degummed oil. The monomolecular rate constant (K_M), calculated from the peroxide values (Table II) for the raw peanut oil decreased with RH and was as low as 0.50×10^{-3} meq O_2/kg/hr at 90.5% RH. In the phosphoric acid degummed oil, K_M values increased with RH recording a value as high as 6.65×10^{-3} meq O_2/kg/hr at 90.5% RH.

The oxygen uptake studies (Table III) confirmed that raw peanut oil had a very long induction period at 90.5% RH, and the rate of autoxidation was slow and K_M values decreased as RH increased.

The total phospholipid content of raw peanut oil was 0.50% (Table I). The oil degummed with water and phosphoric acid had a phospholipid content of 0.1% and 0.06%, respectively. Addition of water washed gums to water degummed peanut oil appreciably reduced the rate of autoxidation (Table II). There was an appreciable rise in the free fatty acid (FFA) content of raw peanut oil stored at high RH's (Table IV) compared to phosphoric acid degummed oil. The reason for this is not clear.

TABLE III

Effect of Relative Humidity (RH) on Oxygen Absorption and Monomolecular Rate Constants in Raw Peanut Oil Autoxidized at 37 C

RH (%)	O_2 absorbed during storage period (wk)[a]					$K_M \times 10^{-3}$ (meq O_2/kg/hr)
	1	2	4	6	10	
2	6.2	9.2	22.3	37.4	68.8	4.03
22	3.3	3.9	8.6	17.2	44.8	3.21
50	3.6	3.6	6.8	16.9	34.9	2.72
67	3.1	3.3	6.8	13.0	37.0	2.82
92	0.0	0.0	0.0	0.2	0.5	0.27

[a]As peroxide value (meq O_2/kg).

TABLE IV

Changes in Free Fatty Acids of Raw and Degummed Peanut Oil Stored at 40 C[a]

Storage period (wk)	Free fatty acid value (as % oleic acid)									
	Raw peanut oil at RH (%)					Peanut oil degummed using phosphoric acid at RH (%)				
	2	20	47.5	67	90.5	2	20	47.5	67	90.5
5	0.6	0.6	0.8	0.8	1.0	0.6	0.6	0.7	0.8	0.9
10	0.6	0.8	1.0	2.1	4.0	0.6	0.6	0.8	0.8	1.2

[a]The initial FFA of raw and phosphoric acid degummed peanut oils were 0.86 and 0.58%, respectively.

From the above data it was evident that the low peroxide value in raw peanut oil at high humidities was not the result of decomposition of the peroxides formed; the gums or phosphatides had an appreciable protective effect against autoxidation of the oil, and this protective effect increased with RH. Also, removal of the phosphatides-gums from the oil by the usual degumming steps adversely affected the stability of the oil stored at high humidities. Phosphatidylcholine, phosphatidylethanolamine and phosphatidylinositol are the phospholipids present in raw peanut oils (6).

The present study indicates that gums rich in phospholipids and glycolipids could be used as antioxidants for some oils, especially when maintaining high relative humidity in the atmosphere above the oil. The fact that antioxidant

efficacy of phosphatides-gums increases with relative humidity suggests that they could be very effective antioxidants, particularly in intermediate moisture foods. The K_M values (Table V) show that the water washed gums give the oil lower rate constants than BHT at high RH's, and α-T had a slight prooxidant action at the RH's studied. As regulations restrict the use of synthetic antioxidants, phosphatides-gums could be an acceptable natural replacement in some applications for synthetic antioxidants currently in use.

TABLE V

Effects of Antioxidants and Peanut Oil Water Washed Gums on the Monomolecular Rate Constants of Peanut Oil Oxidizing at 40 C

Sample	$K_M \times 10^{-3}$ (meq O_2 /kg/hr) at RH (%)		
	2	47.5	90.5
Refined peanut oil	5.04	4.93	4.54
Refined peanut oil + propyl gallate	1.00	0.91	0.68
Refined peanut oil + butylated hydroxy toluene	2.28	3.60	4.15
Refined peanut oil + α-tocopherol	5.20	–	5.6
Raw peanut oil	2.54	1.83	0.50
Degummed peanut oil	5.42	–	2.98
Degummed peanut oil + peanut oil water washed gums	4.12	–	2.05

Although the mechanism of antioxidant action of phospholipids in oils and fats is attributed to the chelation of trace metal catalysts (7,8), their action still remains unanswered in a system which is free from trace metal catalysts, and no visual browning of the phospholipid occurs. The mechanism of the action of phosphatides and gums and the antioxidant action of individual phospholipids at high RH's need further study.

ACKNOWLEDGMENT

B.L. Amla provided encouragement during the course of this investigation.

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[Received October 22, 1984]

Distribution of Major Chemical Constituents and Fatty Acids in Different Regions of Coconut Endosperm

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ABSTRACT

Seven regions of coconut endosperm, comprising four (inner, middle, outer and testa) from the region adjacent to the water cavity to the testa; and three transverse regions from top to bottom, were analyzed for moisture, fat, protein, non-protein nitrogen, soluble sugars, reducing sugars, fiber, total ash and acid insoluble ash. The fat extracted from these regions was analyzed for fatty acid composition and chemical characteristics. A marked gradient in the concentration of major constituents was observed across the endosperm, from the inner region enclosing the water cavity through middle and outer regions and testa, the gradation being more striking for moisture fat and soluble sugars. Fatty acids 6:0 to 12:0 were concentrated in the inner regions, and their contents decreased toward the outer regions with a corresponding increase in the higher acids and unsaturated fatty acids. The chemical characteristics of the fat (Reichert value, Polenske value, iodine value and saponification value) from these regions were found to be compatible with the fatty acid profile. The distribution of the constituents in the transverse regions of the coconut endosperm was fairly uniform.

INTRODUCTION

Coconut palm (*Cocos nucifera* Linn) is the world's principal source of lauric fat. Apart from fat, coconut kernel (endosperm) yields a variety of ingredients for culinary usage. In spite of its economic importance, particularly to the coconut growing countries, information on the chemistry of coconut endosperm is incomplete and often confined to fat because of its commercial importance (1-3). Krishnamurthy et al. (4) reviewed the composition and nutritive value of coconut products in 1958, and since then no comprehensive report has been published on the subject.

Fresh coconut consists of a central water cavity containing coconut water or liquid endosperm surrounded by the white solid endosperm followed by the protective shell and husk. It is generally believed that the chemical constituents are uniformly distributed throughout the coconut endosperm. No concrete evidence exists in the literature to prove the contrary. Earlier attempts by Kartha and coworkers (5-7) revealed only a marginal difference in the quality of the fats extracted from the top, central and bottom regions of the coconut. It is also known that the paring oil (a by-product of desiccated coconut) extracted from the residue comprising testa and a portion of the endosperm adjacent to it, has higher iodine and lower saponification values compared to ordinary coconut oil (8). Recently, Heathcock and Chapman (9) used electron microscopy and observed a marked gradation of cell size, shape and contents between the inner and outer regions of the endosperm. With these exceptions, the idea of quantitative approach to the re-