

Lipid Oxidative Stability of Reconstituted Partially Defatted Peanuts¹

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ABSTRACT

Changes in tocopherol content, peroxide value and fatty acid composition were measured during storage of reconstituted partially defatted peanuts. These values were compared with those of unreconstituted partially defatted peanuts, whole peanuts and the corresponding oils. Reconstitution effectively inactivated the enzyme lipoxygenase and was destructive on tocopherols, particularly α -tocopherol. The stability of the oil during storage, as measured by the peroxide value, is much greater within the peanuts than in the corresponding extracted oil. No changes in fatty acid composition could be observed in reconstituted partially defatted peanuts. A need for immediate reconstitution following mechanical oil extraction could not be demonstrated as both products had equal oxidative stability.

Key Words: Partially defatted peanuts; Peroxide Value, Tocopherol, Oxidative stability.

Partially defatted peanuts are made by three mechanical operations: pressing, reconstitution and drying (24). Reconstitution, consisting usually of immersion in hot water (18) for a few minutes, is intended to swell the pressed peanuts to their original shape and size. 2 to 4% of solubles, mainly sugars and proteins are lost. According to Neucere and Henserling (16), hot water reconstitution reduces protein solubility and inactivates trypsin inhibitors.

Peanuts contain active lipoxygenase (5, 25). During oil extraction by mechanical pressing, the subcellular organelles and membranes of the original peanuts are progressively ruptured (16), possibly promoting an interaction between lipoxygenase and oil. Reconstitution could be an effective means of lipoxygenase inactivation, but the necessity of immediate reconstitution should be weighed against other effects of the process.

The purpose of this work was to study the effect of reconstitution of partially defatted peanuts and compare their tocopherol and oxidative stabilities to those of whole peanuts and the corresponding oils during storage.

Materials and Methods

The seed quality, shelled peanuts, obtained from Gold Kist Peanuts, Anadarko, Oklahoma in February 1977, were stored in sealed containers at -25 C until needed. Partially defatted peanuts (PDP) were prepared by pressing 600 g of blanched Spanish peanuts in a 8.89 cm cylind-

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er outfit in a Carver hydraulic press at 211 kg/cm² for 30 minutes. The oil content of the pressed peanuts was about 25% whereas blanched whole peanuts (BWP) contained about 48% oil. Pressed peanuts were reconstituted (RPDP) in 2.5 times their weight of boiling water for 6 minutes and dried at 50 C for 18 hours to their original moisture content. Oil samples from whole (WPO), partially defatted (PDPO) and reconstituted partially defatted (RPDPO) peanuts were obtained by extraction with 2:1 chloroform-methanol.

All samples were stored in a controlled atmosphere chamber (Controlled Environments, Ltd., Winnipeg, Manitoba) at 50 C and 32% R. H. Two 500 g batches of each type of peanuts were stored in polyethylene bags of 0.00254 cm thickness. Two 50 ml samples of each corresponding oil were kept in 3 cm i.d. open test tubes. Every 4 days, 15 g peanuts from each of the two bags were combined and mixed, as were 0.5 ml of oil from each tube. Peroxide values (PV) and total tocopherol were determined every 4 days, individual tocopherols and fatty acids every 8 days. All analyses were in duplicate.

Peroxide values were determined by the ferric thiocyanate method using isooctane in place of benzene, as proposed by Adnan. (1). Lipoxygenase activity was assayed by the method of Mitchell and Malphrus (15), with linoleic acid as the substrate. Total tocopherol was determined by the method of Low and Dunkley (14) and calculated as α -tocopherol. Individual tocopherols were assayed by separating trimethylsilyl derivatives of non-saponifiable matter by Gas-Liquid Chromatography (GLC) as proposed by Rao and Perkins (21). In addition to GLC, the identity of tocopherols was confirmed by one and two dimensional Thin Layer Chromatography. In both cases, identifications were made against authentic standards. Fatty acids composition was determined by GLC of methyl esters. The method of Christopherson and Glass (4) was used for methylation and identifications were made by retention time comparisons with authentic standards. Concentrations were calculated as peak area percent of the total peak area. Oil samples when required for analyses were obtained by extracting with 2:1 chloroform-methanol.

Results and Discussion

The moisture content (Motomco moisture tester) decreased during 44 days of storage from 7.12 to 4.96% in BWP; 8.24 to 5.23% in PDP; and 6.43 to 5.24% in RPDP.

Figure 1 indicates that as measured by PV, the stability of the oil within the peanuts is greater than that of the corresponding extracted oil. The lipoxygenase activity was 0.62 and 15.79 Abs. units per gram of RPDP and PDP, respectively, but produced no measurable differences in PV. The relatively low lipoxygenase activity in PDP was due to the extended frozen storage of the peanuts. As assays were performed over a 24 month frozen storage period, the activity progressively decreased from 36 Absorbance units per gram of defatted peanuts to the above levels. Reconstitution effectively inactivated the enzyme. Loss of peanut lipoxygenase activity during low temperature storage, even below 0 C, as well as heating above 40 C has been reported by St. Angelo and Ory (26). The low PV in the peanut samples is not believed to be due to hydroperoxide decomposition during solvent evaporation. In one case, the results were confirmed with a sample obtained by mechanical pressing rather than solvent extraction.

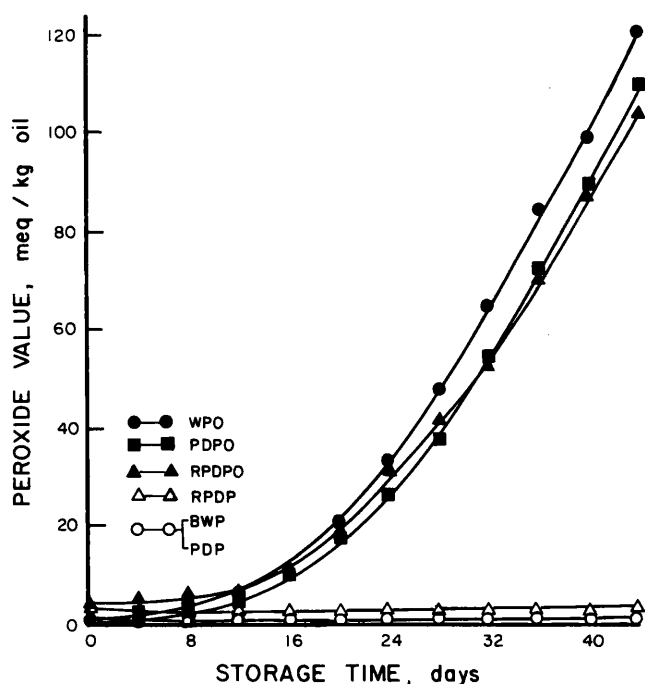


Fig. 1. Peroxide Values of indicated samples during storage at 50 C.

Although WPO had a shorter induction period than PDPO and RPDPO, about 14 as opposed to 16 days, the difference does not seem to be significant. The better stability of the oil retained in the peanut cells could be due either to the lower penetrability of atmospheric oxygen into the spherosomes or the ability of other components in the tissue, such as proteins, to protect it.

Figure 2 gives the rate of tocopherol destruction during the storage period. Destruction in the oil samples is more rapid, although RPDP appear to have behaved anomalously in the first 8 days when they lost 38% of the tocopherol. It is believed that diffusion of atmospheric oxygen along with the penetrating water during reconstitution is responsible. Since the water is removed before the start of the storage period, it is not expected to be responsible, but the oxygen apparently remains. When it is exhausted, the destruction rate continues comparably to other peanut samples.

Komoda and Harada (10) found that addition of water to raw soybeans causes extensive oxidation of tocopherol within 7 days. In this case, however, it may have been due to both oxygen penetration and peroxide formation.

When the data pertaining to the oils from figures 1 and 2 are combined, they demonstrate that tocopherol destruction is accelerated following the induction period. This implies that in oil samples, peroxides destroy tocopherol. The rate of tocopherol destruction in autoxidized lipids is believed to depend on the type of hydroperoxides (7, 13) and to decrease with increasing unsaturation. Thus, the destruction of tocopherol proceeded by a different mechanism in oil than in peanuts.

A number of investigators (2, 6, 11, 19, 22) have reported that only α - and γ -tocopherol are present in Spanish

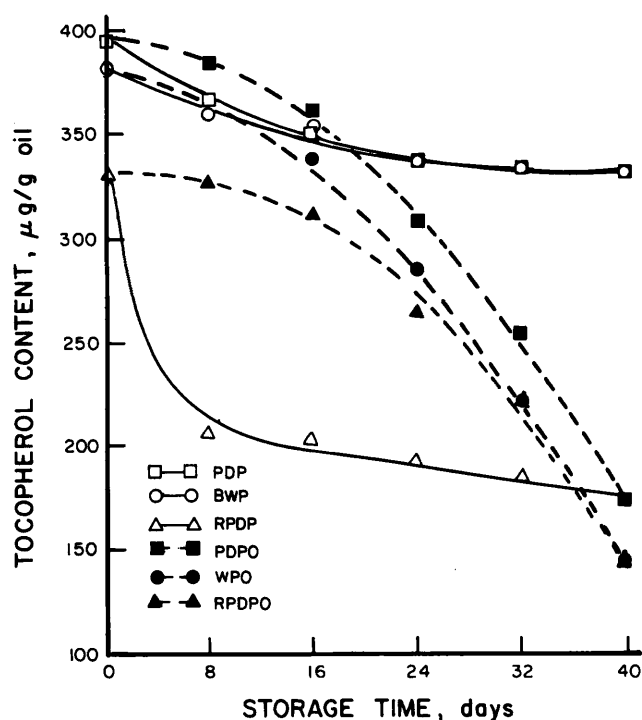


Fig. 2. Total tocopherol content of indicated samples during storage at 50 C.

peanut oil. The same results were obtained here. The γ -tocopherol content of the pressed oil and the oil retained by PDP was higher than that of α -tocopherol by an average ratio of 16:9.

The most labile tocopherol is the α form (2, 12, 23) and figure 3 confirms the more rapid destruction of α -tocopherol. About 28% of α -tocopherol in both BWP and PDP and 3% of γ -tocopherol in BWP and 8% in PDP were destroyed after 40 days of storage. In RPDP, more than 95% of α - and about 27% of γ -tocopherol were destroyed. Re-

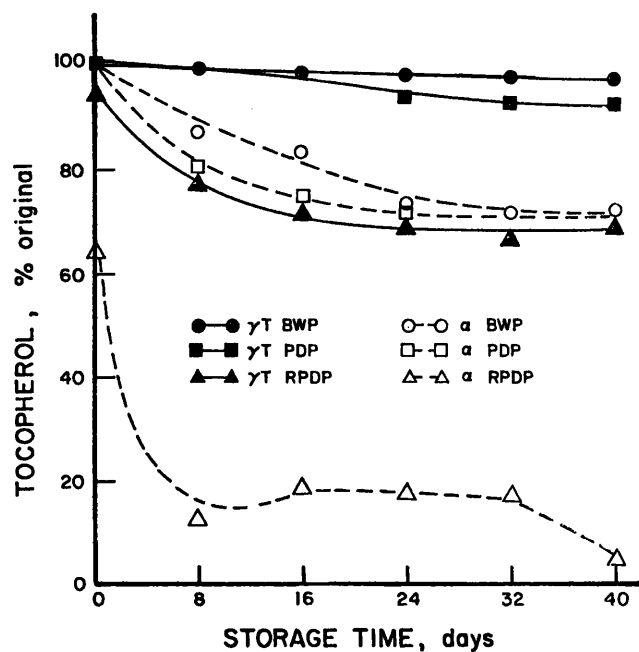


Fig. 3. Per cent destruction of individual tocopherols in indicated samples during storage at 50 C.

constitution alone destroyed 35% of α - and 4% of γ -tocopherol.

The relative activity of individual tocopherols as antioxidants usually has been investigated independently from their stability toward oxidation. A relationship between the two properties has not been established. Reports (8, 17, 20) have indicated that γ - is a more effective antioxidant than α -tocopherol, particularly at higher than physiological temperatures [50C or above] (9). If these conclusions are correct, the effectiveness of tocopherols as antioxidants is not related to their disappearance from the sample. The relationship may be more complex in that the tocopherols, and perhaps γ -tocopherol in particular, may be regenerated by other hydrogen donors in the system. This would be consistent with the observations in this study, but additional research is required to confirm this mechanism.

No changes in fatty acid composition could be observed in any samples including RPDPO which after 44 days of storage had a PV of 105 meq/kg of oil. C_{18:1} averaged $39.85 \pm 0.25\%$ and C_{18:2}, $36.4 \pm 0.4\%$ over the entire storage period. Actually, only a small proportion of the oil was oxidized and considerably higher PV's would be required to produce detectable alterations in the fatty acid pattern.

Literature Cited

- Adnan, M. 1980. Lipid properties and stability of partially defatted peanuts. Ph. D. thesis, University of Illinois, Urbana-Champaign.
- Carpenter, D. L., J. Lehmann, B. S. Mason and H. T. Slover 1976. Lipid composition of selected vegetable oils. *J. Am. Oil Chem. Soc.* 53:714-718.
- Chow, C. K. and H. H. Draper 1974. Oxidative stability and antioxidant activity of the tocopherols in corn and soybean oils. *Int. J. Vit. Nutr. Res.* 44:369-403.
- Christopherson, S. W. and R. L. Glass 1969. Preparation of milk fat methyl esters by alcoholysis in an essentially non alcoholic solution. *J. Dairy Sci.* 52:1289-1290.
- Dillard, M. G., A. S. Henick and R. B. Koch 1960. Unsaturated triglyceride and fatty acid lipoxylase activities of Navy Beans, Small Red Beans, Peanuts, Green Peas and Lima Beans. *Food Res.* 25:544-553.
- Fore, S. P., N. J. Morris, C. H. Mack, A. F. Freeman and W. G. Bickford 1953. Factors affecting the stability of crude oils of 16 varieties of peanuts. *J. Am. Oil Chem. Soc.* 30:298-301.
- Frankel, E. N., C. D. Evans and C. J. Cowan 1957. Determination of tocopherol in oxidized fats. *J. Am. Oil Chem. Soc.*, 34:544-546.
- Ikeda, N. and Fukuzumi 1977. Quantitative analysis of tocopherols in autoxidized methyl linoleate. *J. Japan Oil Chem. Soc.*, 26:343-349. In: *Food Sci. Techn. Abstr.* 1978, 10:2A 133.
- Johnson, F. C. 1971. A critical review of the safety of phenolic antioxidants in foods. *CRC. Crit. Rev. Food Tech.* 2:267-304.
- Komoda, M. and I. Harada 1969. A dimeric oxidation product of γ -tocopherol in soybean oil. *J. Am. Oil Chem. Soc.* 46:18-22.
- Lambertsen, G., H. Myklestad and O. R. Braekkan 1962. Tocopherol in nuts. *J. Sci. Fd. Agric.* 13:617-620.
- Lehmann, J. and H. T. Slover 1976. Relative antioxidative and photolytic stabilities of tocols and tocotrienols. *Lipids* 11:853-857.
- Lips, H. J. 1957. Stability of d- α -tocopherol alone, in solvents and in methyl esters of fatty acids. *J. Am. Oil Chem. Soc.* 34:513-515.
- Low, E. and W. L. Dunkley 1971. Separation of interfering compounds in the determination of tocopherol in milk. *J. Dairy Sci.* 54:1699-1701.
- Mitchell Jr., J. H. and R. K. Malphrus 1977. Lipid oxidation in Spanish peanuts. The effect of moist heat treatments. *J. Food Sci.* 42:1457-1461.
- Neucere, N. J. and T. Hensarling 1973. Immunochemical and cytological study of protein from partially defatted peanuts. *J. Agric. Fd. Chem.* 21:192-195.
- Parkhurst, R. M., W. A. Skinner and P. L. Sturm 1968. The effect of various concentrations of tocopherols and tocopherol mixtures on oxidative stability of a sample of lard. *J. Am. Oil Chem. Soc.* 45:641-642.
- Pominski, J., H. M. Pearce Jr. and J. J. Spadaro 1970. Factors affecting water solubles of partially defatted peanuts. *Food Tech.* 24:76-79.
- Rao, M. K. G., S. V. Rao and K. T. Achaya 1965. Separation and estimation of tocopherols in vegetable oils by thin layer chromatography. *J. Sci. Fd. Agric.* 16:121-124.
- Rao, M. K. G. and K. T. Achaya 1967. Role of tocopherol as an antioxidant in safflower oil. *Fette, Seifen, Anstrichmittel*, 67:711-714. In: *Bio. Abstr.* 1968. 49:44310.
- Rao, M. K. G. and E. G. Perkins 1972. Identification and estimation of tocopherols and tocotrienols. *J. Agric. Fd. Chem.* 20:240-245.
- Slover, H. T., J. Lehmann and R. J. Valis 1969. Vit E in Foods. Determination of tocols and tocotrienols. *J. Am. Oil Chem. Soc.* 46:417-420.
- Slover, H. T. and J. Lehmann 1972. Effect of fumigation on wheat in storage. IV. Tocopherols. *Cer. Chem* 49:412-415.
- Spadaro, J. J. 1969. New uses and products of peanuts. *J. Amer. Peanut Res. and Educ. Assoc.* 1:13-19.
- St. Angelo, A. J. and R. L. Ory 1975. Effect of lipid peroxidation during storage in raw and roasted peanut protein. *Peanut Sci.* 2:41-44.
- St. Angelo, A. J. and R. L. Ory 1972. In symposium: Seed Proteins. G. E. Inglett, Editor, The AVI Publishing Co., Inc., Westport, Conn., pp. 284-291.

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