• *Technical*

The Effect of Various Concentrations of Tocopherols and Tocopherol Mixtures on the Oxidative Stability of A Sample of Lard

R. M. PARKHURST, W. A. SKINNER and PRISCILLA A. STURM,
Life Sciences Research, Stanford Research Institute, Menlo Park, California 94025

Abstract

A comparison was made of α-, γ-, and δ-tocopherol at various concentrations and a mixture of these tocopherols representing the average tocopherol content of peanut oil on the oxidative stability of lard at 97C. Uptake of oxygen was used to indicate the length of the induction period. The antioxidant effectiveness of the tocopherols was found to increase in the order α, δ, γ. The antioxidant efficiency decreases with increasing concentrations of tocopherols such that addition of any single tocopherol above a concentration of 250 μg/g has little effect on oxidative stability. A mixture equivalent to that of an average peanut oil sample, containing 150 μg/g of α-tocopherol and 250 μg/g of γ-tocopherol and 15 μg/g of δ-tocopherol was found to be no more stable than one containing 250 μg/g of γ-tocopherol alone.

Introduction

DURING OUR INVESTIGATION of the factors affecting the oxidative stability of peanut oil (1,2), we confirmed the observations of Fore et al. (3), that there was no simple relationship between tocopherol content and oil stability. Swift, Rose and Jamieson (4) showed that the efficiency of α-tocopherol, as an antioxidant for fatty methyl esters, decreased with increasing concentrations. Studies on the effects of α-tocopherol as an antioxidant were extended by others to include various fats and oils at different temperatures (5,6). Bailey et al. (7), studied the antioxidant effects of adding a mixture of tocopherols, obtained from peanut oil by molecular distillation, back to the oil at various concentrations. The tocopherol mixture, however, was not well-defined chemically. Stern et al. (8), showed that the tocopherols increased in their ability to protect vitamin A acetate and β-carotene in the order α, β, γ, δ. Griewahn and Daubert (9) showed that this order also held for their ability to protect lard at 100C. The work was carried out, however, by using only two concentrations of each tocopherol, and with two different lard samples.

The present work describes the relationship of varying concentrations of α-, γ-, and δ-tocopherol and mixtures of these tocopherols on the oxidative stability of a sample of lard at 97C under carefully standardized conditions.

Experimental

Reagents

The tocopherol stripped lard was obtained from General Biochemicals, Chagrin Falls, Ohio. Analysis showed the product to have no more than 2 μg/g total tocopherols and less than 0.6 meq peroxide/kg. The fatty acid composition was myristic, 0.7; palmitic, 25.3; stearic, 13.1; arachidic, 0.1; palmitoleic, 2.0; oleic, 51.0; linoleic, 5.3; C_{20}-polyethenoic, 2.5 and C_{22} polyethenoic, 2.5. The α-tocopherol was obtained from Merck and Co.; the other tocopherols were obtained from Hoffmann-LaRoche and purity checked by thin-layer chromatography. The lard was melted and degassed in a vacuum and stored in the dark under nitrogen at 0°C.

The tocopherols were added as ethanol solutions and the ethanol was removed in vacuo. The melted sample (0.5 ml) was placed in a Warburg flask which had been cleaned by boiling with aqueous Alconox overnight, washed, allowed to stand in sulfuric acid-nitric acid (1:1) mixture for several hours, washed in distilled water and dried in an oven at 120C. The flask was attached to the Warburg manometer and placed in an oil bath at 97C ± 0.25C. Fifteen minutes were allowed for the flask to attain temperature equilibrium before closing the air cock to the manometer. The relative pressure was recorded periodically.

Results and Discussion

The relative pressure change during the course of the oxidation increased rapidly after an induction period. The end point of the induction period was chosen as the point at which the tangent to the oxidation curve crossed the abscissa in hours. The reproducibility of the procedure was assessed from a series of 26 determinations on a single sample which had an induction period of 4.48 hr with ±.19 hr for one standard deviation.

Fig. 1 shows the induction period in hours vs. the tocopherol concentration in μg/g for α-, γ-, and δ-tocopherol. These data show that tocopherol in excess of 250 μg/g has very little effect in extending the induction period of the lard sample. Both γ- and δ-tocopherol are significantly better antioxidants than α-tocopherol because a given concentration will protect the lard sample approximately twice as long as the same concentration of α-tocopherol. Also, γ-tocopherol is slightly better than δ-tocopherol in these tests. Other workers (8,9), found that δ- was slightly better than γ- under other conditions and when a different method of determining the end point of the induction period was chosen.

The effect of a known mixture of tocopherols under the same conditions of oxidation was also determined. A sample containing 150 μg/g α-tocopherol, 250 μg/g γ-tocopherol and 15 μg/g δ-tocopherol (Table I) was chosen because it represents the approximate average content of tocopherols in peanut oil. The addition of an additional 25 μg/g of γ-tocopherol to this mix-

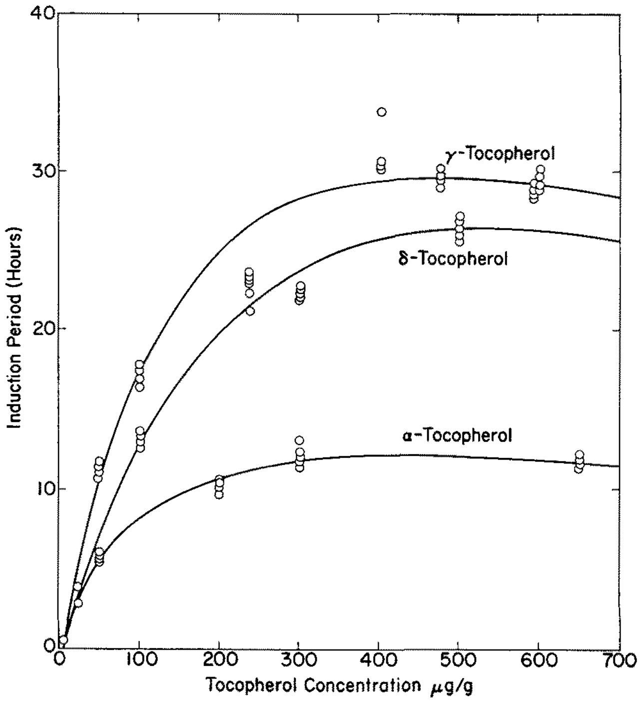

FIG. 1. Induction period vs. tocopherol concentration in lard at 97C.

ture did not change the induction period within the experimental error; and this was also true when pure γ-tocopherol replaced the other tocopherols in this mixture. The 25 $\mu g/g$ of γ-tocopherol was chosen because it represents about two standard deviations in the determination of γ-tocopherol in peanut oil.

The causes for differences that have been found in the oxidative stability of peanut oils are not likely to be found in the small differences in tocopherol content. This conclusion emphasized the need for additional study of other possible causes, such as metal ion contaminants, unsaturated fatty acids, non-tocopherol antioxidants, and antioxidant synergists.

TABLE 1
Induction Period for Lard Containing Various Tocopherols

Tocopherol ($\mu g/g$ oil)			Induction period (hr:min)
α	γ	δ	
150	250	15	28:20, 28:35, 29:00, 29:15, 29:30, 26:00, 27:10, 26:50, 27:30, 28:10. Avg: 28:02 ± 1:08
150	275	15	27:30, 27:40, 27:45, 27:50, 28:00, 25:10, 26:00, 26:50, 27:30, 27:30. Avg: 27:11 ± 0:17
415	0	0	12:00
0	415	0	28:40
0	0	415	25:00

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