Changes in the Tocopherol Content of Almond, Pecan and Macadamia Kernels During Storage

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The individual tocopherols present in almond, pecan and macadamia nuts were determined by HPLC. Changes in tocopherol content during 16-months' storage at 30°C and 55% relative humidity were related to keeping quality. The large amount of total tocopherols, mainly α-tocopherol, in almonds accounted for their good storage ability. Pecan nuts with less total tocopherols and mainly γ-tocopherol became rancid after 4 months' storage and macadamia nuts, with practically no tocopherols, were rancid after 2 months' storage. Total tocopherol content decreased in all nuts during storage, possibly as a result of its inhibitory function during auto-oxidation.

The most important natural antioxidants in fats and oils are tocopherols. They also exhibit vitamin E activity which is important nutritionally (1). Eight natural compounds possess vitamin E activity, namely α-, β-, γ-, δ-tocopherols (2) and four closely related tocotrienols (3). The latter compounds occur at much lower levels and their structures differ from tocopherols in that they have three double-bonds in the side chain (4). The highest level of vitamin E activity comes from α-tocopherol and a need for it exists in the diet when an excess of polyunsaturated fats is consumed (5).

At temperatures between 25° and 35°C, the antioxidant activities of α- and γ-tocopherols are similar, but under certain conditions the latter may be the more effective antioxidant (6). Tocopherols are also easily oxidized and particularly γ-tocopherol is readily oxidized to chroman-5-6-quinone, which has poor antioxidant characteristics. A fat exposed to oxygen becomes rancid according to the rate at which its antioxidants are destroyed under the conditions of storage (6).

At 97°C the antioxidant efficiency of tocopherols decreases with increasing concentration. A single tocopherol concentration of more than 250 μg/g had little effect on oxidative stability (7).

Qualitative and quantitative determinations of compounds related to auto-oxidation can lead to reasonable predictions regarding the stabilities of oils (4). Almonds, with a mean value of 27.4 mg/100 g tocopherol, are rated one of the most important sources of α-tocopherol. However, they contain only low concentrations of γ-tocopherol. Pecan nuts contain more γ-tocopherol and less α-tocopherol than almonds. No other tocopherols were detected in these nuts (5). No published data for tocopherol content of macadamia nuts could be found.

The objectives of this study were to quantify the main individual tocopherols present in almond, pecan and macadamia nuts by a rapid and selective method, to investigate possible changes in content during storage and to establish if keeping quality is related to these changes.

EXPERIMENTAL PROCEDURES

Materials. Shelled pecan (Moore), macadamia (Nelmar) and five almond cultivars (Burbank, Peerless, Ne Plus Ultra, Ai and Davey) were used.

Method. Whole kernels were stored in open plastic trays at 30°C and with a relative humidity of 55%. Samples (250 g) were randomly collected bimonthly. Triplicate samples (7 g) were defatted with petroleum ether by Soxhlet extraction (16 h) to obtain oil for tocopherol determinations. Samples (100 g) were ground and used for sensory evaluation. Whole, shelled kernels of each nut were stored at −30°C in double plastic bags as standards for sensory evaluation. Rancidity was determined with the triangular test (8) and the significance was calculated according to the tables of Roessler *et al.* (9). A modification of the method described by Carpenter (4) was used to determine individual tocopherols. HPLC was performed with a Varian 5030 Gradient HPLC equipped with a Varian UV 100 detector (295 nm) and a Micropak column. Iso-propyl alcohol (1.5% v/v) in hexane was the eluent.

External standards. DL-α-tocopherol (Merck) and γ-tocopherol (Roche Products) were standards.

RESULTS AND DISCUSSION

No significant differences ($P>0.05$) regarding rancidity were detected by the taste panel in almonds after 16 months' storage. These results proved the good storage ability of almonds (10). In pecan nuts significant differences ($P<0.001$) regarding rancidity were detected after 4 months' storage and in macadamia nuts after 2 months' ($P<0.01$) and 4 months' ($P<0.001$) storage. Pecan and macadamia nuts had poor storage properties under these conditions. Howes (11) showed that pecan and macadamia nuts could not be stored for long periods at room temperature without becoming rancid.

The α-tocopherol content of almonds varied between 28.4 and 41.4 mg/100 g oil. The maximum values for pecan and macadamia nuts were 1.8 and 2.5 mg/100 g oil respectively. Found in pecans (12.3 to 17.4 mg/100 g oil) was γ-tocopherol and it also was found in almonds (0.9 to 3.2 mg/100 g oil), while trace amounts occurred in macadamias. Other tocopherols only occurred in trace amounts. These results confirmed those of Lambertsen *et al.* (5). The α- and γ-tocopherol content of almond cultivars also varied. Ai was the best source of α-tocopherol, while Davey contained the most γ-tocopherol.

Most studies regarding antioxidant activity were done on model systems of tocopherols and little information is available on the activity in specific products. Swern (6) showed that α-tocopherol and γ-tocopherol

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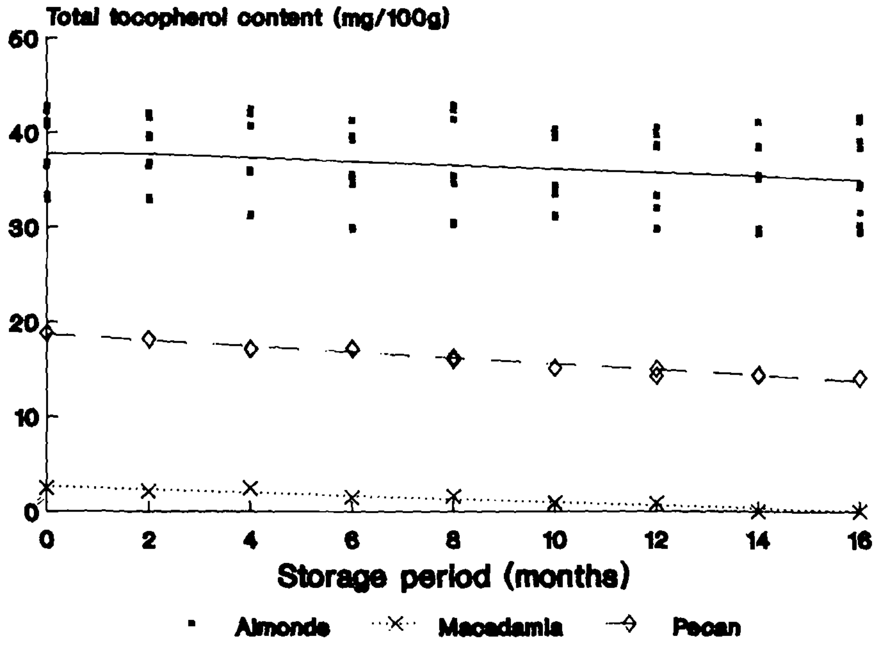

FIG. 1. Changes in the tocopherol content of almond, pecan and macadamia kernels during storage.

have the same antioxidant activities at temperatures between 25° and 35°C. In the present study the nuts were stored at 30°C and it may be assumed that the antioxidant activites of α- and γ-tocopherols were equal. Therefore the individual values for α- and γ-tocopherols could be combined and expressed as total tocopherol content (Fig. 1). The mechanism of antioxidant activity in nuts is unknown and it is postulated that the stability against rancidity depends on unsaturated fatty acid and naturally-present antioxidant contents (6). Before any conclusions can be made regarding stability, a combined study must be done on the tocopherol and fatty acid contents.

In almonds, where oleic acid and linoleic acid are the main unsaturated fatty acids (10), large amounts of α-tocopherol are found. The large amount of total antioxidants readily available over a 16 months' storage period (Fig. 1) may account for the good storage ability of almonds (10), because they prevent autooxidation of fatty acids and therefore no rancidity had been detected.

The main unsaturated fatty acids in pecan nuts are also oleic and linoleic acids (12). Pecan nuts also contain eicosenoic and linolenic acids (13), which oxidize rapidly. Pecan nuts contain less total tocopherols than almonds (Fig. 1) and the tocopherols consist mainly of γ-tocopherol, which has the same antioxidant activity as α-tocopherol, but is readily oxidized to chroman-5-6-quinone, which has poor antioxidant characteristics. This explains the poorer storage ability of pecan nuts (11) and therefore the presence of rancidity after 4 months' storage.

Macadamia nuts, with palmitoleic acid and oleic acid as the main unsaturated fatty acids, also contain large amounts of eicosenoic acid and less linoleic acid (14). In total they contain less unsaturated fatty acids than the other nuts, but they also contain practically no tocopherols (Fig. 1) and are thus most sensitive to auto-oxidation. Rancidity was, therefore, not unexpectedly detected after only 2 months' storage.

The decrease in total tocopherol content of all three types of nuts during storage (Fig. 1) can possibly be explained by the tocopherols acting as hydrogen donors during auto-oxidation to stop the chain mechanism of auto-oxidation. The large amount of natural tocopherols available in almonds can account for the excellent keeping quality of these nuts during a storage period of 16 months' at 30°C.

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