Oil Content and Fatty Acid Composition of Developing Almond Seeds

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Oil content and fatty acid composition were determined in developing almond kernels (*Prunus amygdalus*) at 3-week intervals, from March to September. Three marked stages with different rates of oil accumulation were observed. The major part of oil was stored in a 5–7-week period, approximately 2 months before harvest. Significant variations of fatty acid composition were detected in the three stages cited. High percentages of palmitic, linoleic, and linolenic acids were present at initial stages, followed by a diminution of these acids and a continuous increase of oleic acid.

Almond oil is used mainly for cosmetic, pharmaceutical, and pastry products (Vaughan, 1970; Rugraff et al., 1982). Copious information concerning the oil fraction of ripe almonds exists. Oil content ranges from 50 to 65% dry weight (Souty et al., 1971; Mehran and Filsoof, 1974; Filsoof et al., 1976; Nassar et al., 1977; Riquelme, 1982; Cañellas, 1986). Oleic (59–78%) and linoleic (19–30%) have been reported as the main fatty acids, together with small amounts of palmitic, palmitoleic, stearic, and linolenic acids (Garcia-Olmedo and Marcos-Garcia, 1971; Nassar et al., 1977; Riquelme, 1982; Cañellas, 1986). Variety, climate, and mainly maturity stage are cited as factors affecting the relative fatty acid composition (Cañellas, 1986; Mehran and Filsoof, 1974; Schuster, 1980). Extensive investigations on complete chemical composition of ripe almond, including oil, were previously carried out by Saura Calixto et al. (1981, 1982, 1983, 1984 a,b, 1985). However, few references on composition changes during development of these fruits are to be found (Munshi et al., 1982; Munshi and Suhkija, 1984).

The objective of this paper is to examine the changes in oil content and fatty acid composition of almond kernels during development to maturity.

EXPERIMENTAL SECTION

Samples. The samples used corresponded to the Pons variety, cultivated on the island of Mallorca, Spain, under known climate and culture conditions (Soler, 1986). Samples were collected from 20 selected trees at approximately 3-week intervals and were kept at −20 °C until analysis. The collection extended from March to September in three consecutive years (1982–1984). For quantitative purposes the date of fruit set (time 0) was conventionally considered when the fruits possessed the following dimensions: length 1.1 cm; width, 0.9 cm; thickness, 1.0 cm. Hulls, shells, and tegument of the fruit were first removed. The samples were dried and homogenized.

Oil Extraction. Oil was extracted with diethyl ether in a Soxhlet extractor for 18 h. The extract was filtered and water eliminated with Na_2SO_4. The solvent was removed by vacuum distillation.

Gas Chromatographic Analysis. The oil samples had been previously treated with methanol in half acid, at reflux, for 4 h. For each 100 mg of oil is taken 6 mL of esterification reagent, which is prepared by mixing 57.5 mL of benzene with 172.5 mL of methanol and 2 mL of concentrated H_2SO_4 (Utrilla et al., 1976). Fatty acid methyl esters were extracted with hexane.

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Analyses were carried out by GLC, using a Perkin-Elmer chromatograph, Model Sigma 3B, equipped with a chromatography data station, Model Sigma 10B. The GC possessed a flame ionization detector. A stainless steel column (6 ft × $^1/_8$ in.) containing 10% DEGS impregnated on 80–100-mesh Chromosorb AW was used. Assays were carried out under isothermal conditions. The column, injector, and detector temperatures were 190, 240, and 240 °C, respectively. Nitrogen flow was 30 mL/min with 0.2 μL of sample injected. Identification and quantification of fatty acids were performed by comparing the retention data and the areas of the peaks of standards with samples. The dead volume was determined by the Peterson and Hirsch method proposed by Grobler and Bâlizs (1974). For determinations a homologous series of *n*-alkanes (C_{10}–C_{24}) were injected.

RESULTS AND DISCUSSION

Oil Content. The changes in oil content (percent dry weight) of developing almonds corresponding to the 3 years studied are shown in Figure 1. Variations from ca. 3.5% at the beginning to ca. 61% at harvest were observed. The final values were similar for the three crops. Rates of accumulation were also similar, although some differences were monitored the first year, probably due to the exceptional climate conditions.

Three different periods of development can be observed: from 0 to 70–80 days after fruit set (DAFS) (stage 1) when lipid deposition had barely begun; from 70–80 to 115–125 DAFS (stage 2) corresponding to an active period of lipid accumulation; from 115–125 DAFS until harvest (stage 3) with a slight increase of oil content. The beginning of stage 2 was easily detected because the gelatinous aspect of the seeds becomes creamy white. On the other hand, it must be pointed out that stage 2 coincides with a rapid decline of the water-soluble sugar content, from about 60 to 6% dry weight, previously reported (Saura et al., 1984a).

The results presented in Figure 1 are relative values because the variations of other constituents affect the parallel increase in oil content. Changes in the weight of kernels (average weight of the seed and the contribution of the oil to the increase of the dry weight of kernels) can be seen in Figure 2. On the other hand, a continuous reduction of moisture content took place—from about 90% to 5% (see Figure 3). High moisture content during the first 75 days makes oil accumulation referred to fresh matter less reliable than those observed on the dry sample.

In summary, independent of the system of data expression, the three stages above cited can be observed, and the major part of oil is accumulated in 5–7 weeks, approximately 2 months before harvest.

Fatty Acid Composition. Fatty acid analyses were carried out in the third year of the study. The results are listed in Table I. Some fatty acids detected only at trace level are not included ($C_{12:0}$, $C_{14:0}$, $C_{17:0}$, $C_{17:1}$). The presence

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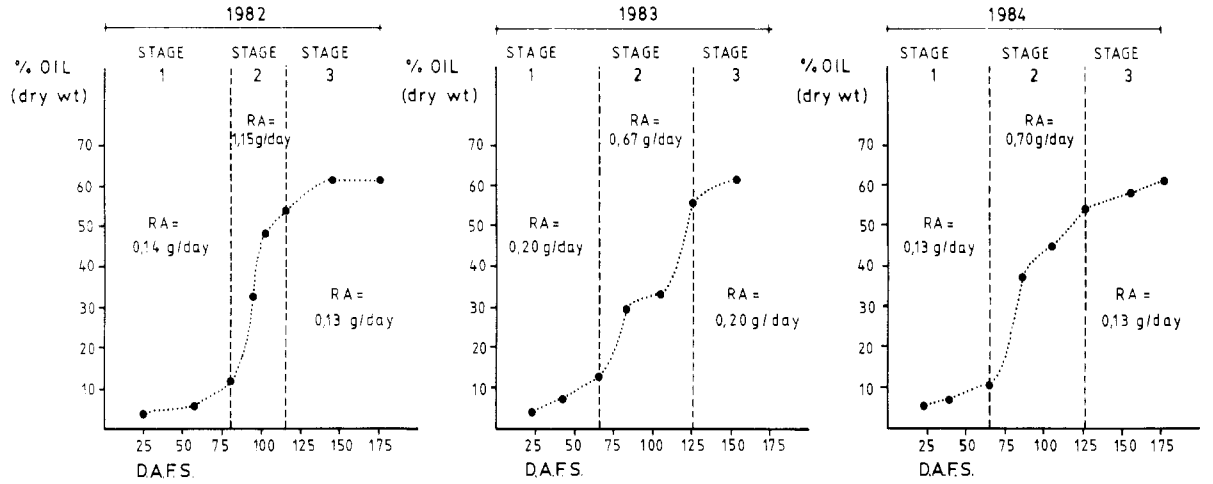

Figure 1. Changes in oil content of developing almonds.

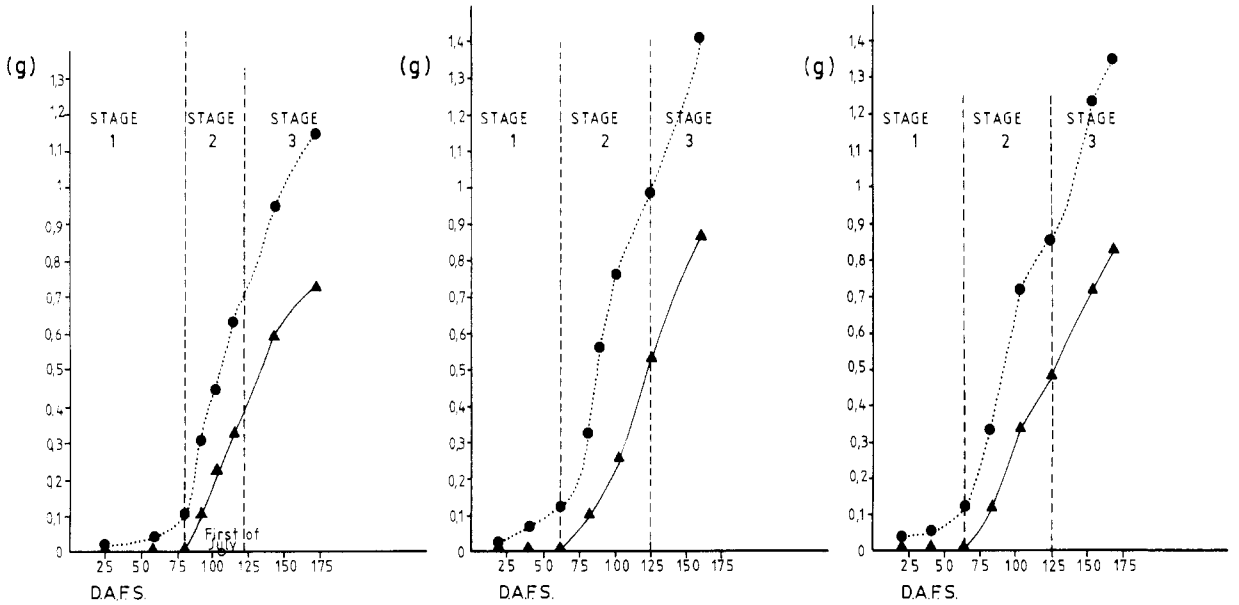

Figure 2. Average weight of one kernel (●) and grams of oil/kernel (▲) of developing almonds.

Table I. Changes in Fatty Acids Composition during Development and Maturation of the Almond Kernel (Values Expressed as Percentages)[a]

DAFS	$C_{16:0}$	$C_{16:1}$	$C_{18:0}$	$C_{18:1}$	$C_{18:2}$	$C_{18:3}$	$C_{20:0}$
23	19.0 ± 0.4	6.0 ± 0.2	3.0 ± 0.1	32.5 ± 0.7	29.9 ± 0.7	8.4 ± 0.2	$1.2 \pm 0.0_3$
40	25.6 ± 0.6	$1.6 \pm 0.0_3$	5.2 ± 0.1	20.4 ± 0.5	35.0 ± 0.9	9.2 ± 0.2	$3.0 \pm 0.0_6$
64	18.5 ± 0.3	$0.8 \pm 0.0_2$	$1.9 \pm 0.0_3$	17.5 ± 0.5	59.2 ± 1.1	$1.4 \pm 0.0_3$	$0.7 \pm 0.0_1$
85	10.0 ± 0.2	$0.1 \pm 0.0_1$	$1.3 \pm 0.0_4$	47.5 ± 0.9	41.1 ± 1.0	tr	
105	9.6 ± 0.2	$0.6 \pm 0.0_2$	$1.9 \pm 0.0_5$	51.4 ± 1.1	36.5 ± 0.9	tr	
126	6.5 ± 0.1	$0.4 \pm 0.0_2$	$1.6 \pm 0.0_6$	57.8 ± 1.3	33.9 ± 1.1	tr	
156	6.8 ± 0.2	$0.5 \pm 0.0_1$	$1.6 \pm 0.0_4$	62.0 ± 1.5	29.1 ± 0.8	tr	
176	6.5 ± 0.1	$0.5 \pm 0.0_1$	$1.5 \pm 0.0_3$	62.5 ± 1.4	29.0 ± 0.8	tr	

[a] Average value ± SD. Number of determinations, 4.

of these fatty acids has previously been detected in the ripe seed by GLC in three different stationary phases (Saura et al., 1985).

It is known that in almonds, as in other oil seeds, phospholipids and glycolipids are first biosynthesized; later, at an intermediate stage, the accumulation of the acylglycerides, a fraction that represents about 95% of oil in mature fruits, begins (Munshi et al., 1982; Shing and Privett, 1970).

When the composition changes with the three developing stages described above are correlated, it can be deduced that the first stage is characterized by a higher concentration of saturated and essential fatty acids, especially linoleic, while during the second stage the percentage of these fatty acids decreased, whereas that of oleic acid increased. At the end of the stage 1, linolenic and arachidic acids practically disappear, coinciding with the time when complete physical growth of the kernels has taken place (maximum weight and size).

No significant changes of composition were observed in the third stage: Only slight variations of oleic and linoleic acids were observed.

High initial concentrations of palmitic, linoleic, and linolenic acids may be related to their incorporation into polar lipids—the main constituents at the beginning—and with the formation of cell walls. Later, when phospholipid

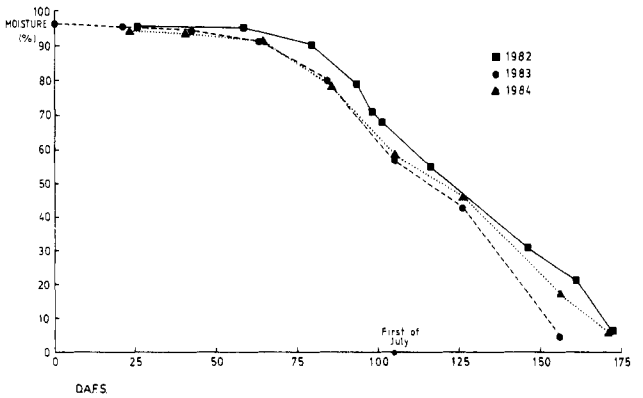

Figure 3. Variations of moisture content.

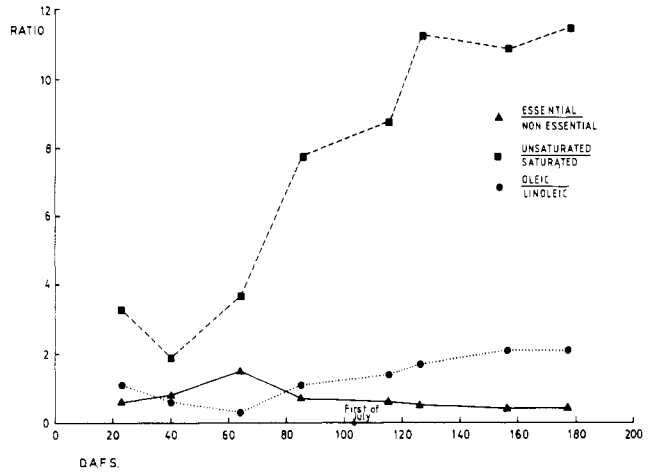

Figure 4. Evolution of some fatty acids rates.

and glycolipid content progressively decreases and acylglyceride content rises, an appreciable percentage diminution of palmitic and linolenic acids is observed. The variation of linoleic acid percentage is different because it is also component of triglycerides.

After the first stage, oleic acid, the main constituent of triglycerides, increased continuously until harvest. The inverse variation of oleic and linoleic acids, observed from 65 DAFS, seems to indicate that the oleic acid content generally increases at the expense of linoleic acid.

Finally, the changes in the ratios of nutritional and technological interest (unsaturated/saturated, essential/nonessential, oleic/linoleic acids) are shown in Figure 4.

During the growth of the seed, the contents of saturated fatty acids decrease, its final value being one-third of the initial one. On the other hand, the unsaturated fatty acids increase, so that the proportion of saturated/unsaturated fatty acids increases considerably, from 3.3 to 11.5. The essential fatty acids present in very high concentrations in the earlier stages decrease in time, which is why, obviously, the quotient essential/nonessential also decreases. Finally, the ratio oleic/linoleic, one of the oil stability markers, begins to increase from 60 DAFS.

Registry No. $C_{16:0}$, 57-10-3; $C_{18:1}$, 112-80-1; $C_{18:2}$, 60-33-3; $C_{18:3}$, 463-40-1.

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