storage heat treatments is substitution for postharvest DPA treatments of apple cultivars susceptible to superficial scald (Lurie et al., 1990). After 3 months in air storage, all heat-treated 'Granny Smith' had less scald than nonheated fruit (Table 3). Heated apples also had a lower concentration of conjugated trienes and  $\alpha$ -farnesene in the cuticle, as has been noted previously (Lurie et al., 1990). Treatment with DPA was still the most effective anti-scald measure, however, since the high-temperature treatments that controlled scald resulted in heat damage (Table 3). This damage was characterized by flesh browning exterior to the vascular bundles and by "patchy" skin browning, which was distinctively different from that of storage scald.

In general, keeping apples at 46 or 42C for 12 or 24 h, respectively, before storage appeared to affect ripeness characteristics in a manner similar to prestorage treatment at 38C for 3 or 4 days. In several instances, 46C for 12 h actually appeared to provide a greater benefit than treatments at lower temperatures for longer periods of time. These results indicate that a shorter period at a higher temperature can duplicate the favorable results obtained previously at 38C for 96 h (Klein and Lurie, 1990a), thus making heat

treatment more energy efficient.

Accumulated heat units (AHU; degreehours >0C) were not correlated with changes in ripeness characteristics. The 542 AHU provided by 46C for 12 h affected softening, acid loss, and ground color changes in a manner similar to the changes produced by 3654 AHU (38C for 96 h). Downs et al. (1989) found that AHU was correlated with ripeness measurements of pears only when the prestorage temperature was ≤20C; correlations at temperatures > 30C were not significant. However, it seems that the superficial scald severity index is more closely linked with AHU, since only the longer incubation times at 46 and 42C inhibited scald as effectively as did 72 or 96 h at 38C. However, these treatments at higher temperature led to heat damage. Recent preliminary tests showed that dipping heated fruit in 3% CaCl<sub>2</sub> before storage synergistically reduced the development of superficial scald, in addition to improving the general keeping quality of the fruit (Klein and Lurie, 1990b). This finding may point the way to more energy-efficient heat regimes that could replace chemical treatments such as DPA dips.

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## **Changes in Pectic Fractions during** Ripening of Cider Apples

J.J. Mangas, E. Dapena, M.S. Rodríguez, and J. Moreno Centro de Experimentación Agraria, Consejería de Agricultura y Pesca del Principado de Asturias, 33300 Villaviciosa, Asturias, Spain

## M.D. Gutiérrez and D. Blanco

Departamento de Química Física y Analítica, Universidad de Oviedo, 33006 Oviedo, Asturias, Spain

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Abstract. Water-soluble pectin (WSP), chelator-soluble pectin (CSP), and hydrochloric acid-soluble pectin (HASP) were monitored in five Asturian apples (Malus domestica Borkh.) throughout ripening. The alcohol-insoluble solid content was found to decrease during ripening, while those of the WSP and CSP fractions increased in the final stages of ripening. This increase was probably at the expense of the HASP content, which had decreased by the end of the ripening period.

Pectins are known to include a rhamnogalacturonan backbone in which 1-4 linked α-D-galacturonan chains are disrupted by kinks arising from L-rhamnopyranosyl residues bearing neutral side chains consisting basically of L-arabinose, D-galactose, and Dxylose (Meurens, 1977; Saulnier and Brillouet, 1988). These neutral sugar side chains tend to form blocks that result in hairy regions (De Vries et al., 1982) and link pectins with hemicelluloses.

The components of the cell wall and middle lamella of the pulp cells in apples undergo significant structural variations during ripening, thus changing the texture of the fruit. Pectic substances, hemicellulose, and cellulose undergo depolymerization in ripening fruits, thereby contributing significantly to tissue softening (Proctor and Peng, 1989). As apples usually soften while ripening, the activity of some enzymes, such as pectinesterase and β-galactosidase, increases

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The changes in the various pectic fractions, i.e., water-soluble (WSP), chelatorsoluble (CSP), and hydrochloric acid-soluble (HASP) pectin, throughout fruit ripening is of interest because the softening of apples is related to the contents of these fractions. They would be especially important if a decrease in the insoluble pectin content (HASP fraction) increased the risk of fruit deterioration as it accumulates and, thus, may favor the penetration of pathogens into the fruit. Similarly, the juice yield of the fruit is determined by its degree of ripeness, and the expressible juice yield is reportedly related to the cleavage of interpolymer bonds, the hygroscopic swelling of the wall, and the softening of the apple cell walls (Knee, 1973).

Soluble pectin plays an active role in the clarification of apple juice, upon which it acts as a protective colloid usually bound to proteins to form electronegative particles (Yamasaki et al., 1964). Its occurence increases the viscosity of the medium, which in turn decreases the sedimentation rate of the particles forming clots during clarifica-

The aim of this work was to monitor pectic fractions (WSP, CSP, and HASP)

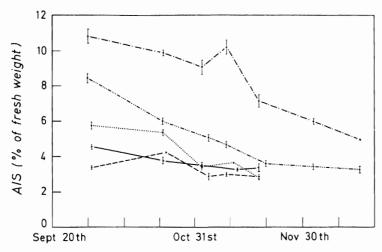


Fig. 1. Variation of the alcohol-insoluble solid (AIS) fraction during ripening of apples 'Picona Rayada' (—), 'Duron Arroes' (— · -), 'Raxao' (— —), 'Collaos' (— · · —), and 'Meana' (· · · · · ·).

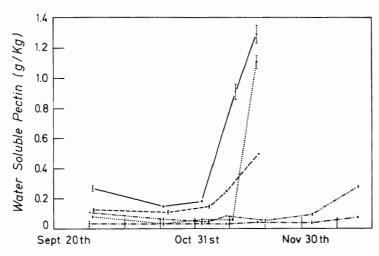


Fig. 2. Changes in the WSP fraction during ripening of apples 'Picona Rayada' (—), 'Duron Arroes' (— · -), 'Raxao' (— -), 'Collaos' (— · · -), and 'Meana' (· · · · ·).

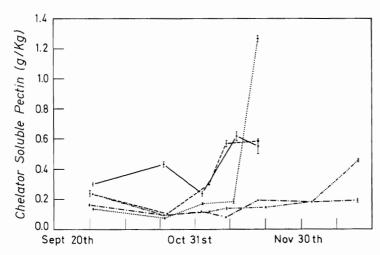


Fig. 3. Changes in the CSP fraction during ripening of apples 'Picona Rayada' (—), 'Duron Arroes' (— · -), 'Raxao' (— -), 'Collaos' (— · · -), and 'Meana' (· · · · ·).

throughout the ripening of five Asturian apple cultivars commonly used in making cider.

Fruit sampling. Specimens of five apple cultivars commonly grown at the Centro de Experimentación Agraria of Villaviciosa,

Asturias, Spain ['Picona Rayada' (bitter-sweet), 'Raxao' (sharp), 'Meana' (bitter-sharp), 'Duron Arroes' (sweet), and 'Collaos' (mild sharp)] were sampled throughout the fruit ripening period on the tree between Sept. and Dec. 1987. The collected specimens were

immediately processed for subsequent analyses

Alcohol-insoluble solids. The alcohol-insoluble solids (AIS) fraction was processed by a method developed at the Station de Recherches Cidricoles et de Biotechnologie Végétale (INRA), Rennes, France. Between 100 and 200 g of apple was blended with boiling ethanol in a 40:60 (w/w) ratio. The mixture then was filtered through a porous glassy membrane (G-3) and washed with two 1-liter portions each of 60% (v/v) ethanol at the boiling point and at room temperature. The filtrate from the latter washing was subjected to the Molish test to check for the absence of soluble sugars in the filtration cake. The residue was allowed to dry overnight at 40C; once dry, its weight was used to evaluate the AIS content of the sample.

Pectic fractions. The extraction of pectin fractions was carried out by a method developed at INRA.

Between 0.6 and 1.0 g of pulverized AIS was sequentially extracted as follows:

1) Water-soluble: The WSP fraction was obtained from three aqueous extractions (240 ml each). Extraction was at 25C with a shaking of 30, 30, and 15 min, respectively. The extracts were made up to 1 liter with distilled water and stored for subsequent analysis.

2) Chelator-soluble: The CSP fraction was also extracted three times at 25C by using 120 ml of 0.75% ammonium oxalate each time and shaking for 30, 15, and 15 min, respectively. The extracts were made up to 500 ml with distilled water before being stored.

3) Hydrochloric acid-soluble: The HASP fraction was extracted with three 240-ml portions of 0.05 M HCl by shaking for 45 min at 85C each time. The extracts were made up to 1 liter with distilled water.

The fractioned pectin was measured as total galacturonic acid according to the methods of Kitner and Van Buren (1982) and Thibault (1979) by incubation with sulfuric acid and subsequent color development with alkaline m-hydroxydiphenyl. The process was monitored spectrophotometrically at 520 nm on a Perkin Elmer Landa 5 instrument (Norwalk, Conn.).

The quantity of AIS decreased throughout ripening in all five apple cultivars studied (Fig. 1). The variations in content were quite small in the final stage of ripening, which is consistent with the stabilization of fruit size during that period and lessens the effect of dilution. The WSP and CSP fractions increased in the final stage of ripening (Figs. 2 and 3). The increase in WSP was particularly marked in 'Meana' and 'Picona Rayada', while the increase in the CSP fraction was substantial in 'Meana'. This different pattern appears to be the result of the enzymatic activity in the final stage of apple ripening that causes the solubilization of structural carbohydrates in the cell wall (Knee, 1973; Proctor and Peng, 1989).

The HASP fraction accounts for by far the greatest part of extracted pectin (Fig. 4). This fraction increases up to the final stage of fruit ripening and then starts to decrease as the

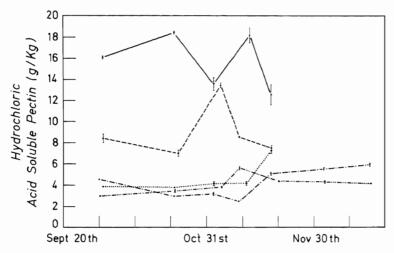


Fig. 4. Changes in the HASP fraction during ripening of apples 'Picona Rayada' (—), 'Duron Arroes' (— · -), 'Raxao' (— -), 'Collaos' (— · · -), and 'Meana' (· · · · ·).

WSP and CSP fractions begin to increase. Thus, a close relationship between WSP, CSP, and HASP fractions is suggested. Also, the decrease in the HASP fraction in the final stage of ripening—particularly in 'Picona Rayada' and 'Raxao'—is larger than the sum of the increases in the WSP and CSP fractions, which prompts the depolymerization of pectic polysaccharides in the cell wall.

The optimal dates for fruit processing of the five cultivars ('Collaos', 5-10 Dec.; 'Meana', 10-20 Nov.; 'Raxao', 1-10 Nov.;

'Picona Rayada', 5-15 Nov.; 'Duron Arroes', 25 Dec.- 5 Jan.) in the 1987-88 vintage were determined by the fructose: malic acid ratio and the starch content (Lugol index). An increase in the WSP fraction and a decrease in the HASP content was detected in these optimal periods.

Our findings suggest that the WSP and HASP contents could be used to determine the optimal date for cider apple processing, because the WSP fraction is readily extracted in fruit processing and thereby influences

technological aspects of clarification and the sensory properties of the cider. Also, the decrease in the HASP fraction of insoluble pectins will affect the quality of the raw material and the amount of expressible juice obtained in fruit milling and pressing.

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