Chemical Compositional Changes in Two Genetically Diverse Cultivars of Mayhaw Fruit at Three Maturity Stages

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The levels of nonvolatile acids, sugars, and pectin and the carbohydrate composition of pectin were determined in two cultivars of mayhaw fruit (Yellow Gem, *Crataegus aestivalis*, and Super Spur, *Crataegus opaca*) at three stages of maturity. Malic acid was the principal acid found in both cultivars and decreased during fruit maturation. Malic acid levels did not decrease as rapidly in Yellow Gem as in Super Spur. Quinic acid also decreased in both cultivars, but the levels were higher in Yellow Gem than in Super Spur at all stages of maturity. Citric acid reached its highest level at the midripe stage in Super Spur and then decreased slightly by the ripe stage. This acid was found in only trace amounts in Yellow Gem at all stages of maturity. Major sugar levels of fructose and glucose increased from the immature to the ripe stage in both cultivars, while sucrose and sorbitol changed very little. Total pectin levels did not change with maturity. However, appreciable changes were observed in pectin carbohydrate composition during maturation. In both cultivars, the arabinose content in pectin decreased, while galacturonic acid increased at the ripe stage.

INTRODUCTION

Mayhaws, members of the *Crataegus* genus, are small berry-like fruit grown primarily in the southeastern United States. The fruit are used in "cottage" industries to produce jellies, jams, wines, and syrups. The major fruit source is from trees grown in the wild, although some cultivated orchards have been in existence for about 5 years (Payne et al., 1990). Recently, there has been interest in improving this crop by breeding for new hybrids and by cultivation. Presently, the levels of nonvolatile acids and sugars have been determined in only ripe fruit, and little is known about how these components change during fruit maturation. The major nonvolatile acids of mayhaw fruit include malic, citric, and quinic, with malic being the principal acid ranging from 1.0 to 2.0% of the fresh weight (Chapman et al., 1991a). Fructose is the major sugar found in mayhaws, and fructose and glucose account for about 3% of the fresh weight in mature fruit. The only other sugar components of any significance are sucrose and the sugar alcohol, sorbitol, which account for only 0.5%. Since one major use for this crop is jelly manufacturing, the pectin levels and pectin carbohydrate composition at different maturity stages would be useful chemical information for improving mayhaw cultivars.

Yellow Gem (*C. aestivalis*) and Super Spur (*C. opaca*) were chosen for this study because the levels of citric and quinic acids were almost reversed and were much different from the levels found in ripe fruit of eight other cultivars (Chapman et al., 1991a). These two cultivars represent the extreme genetic diversity within the 10 mayhaw cultivars thus far analyzed in this laboratory. The purpose of this study was to determine the changes in nonvolatile acids, sugars, and pectin and the carbohydrate compositional changes in pectin in these fruit at three stages of maturity.

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MATERIALS AND METHODS

Fruit Samples. Yellow Gem (*C. aestivalis*) and Super Spur (*C. opaca*) mayhaw fruit were harvested using commercial procedures from trees grown under standard cultivation. A complete harvest was made on all fruit approximately 60–70 days after flowering. The fruit were cooled, packed in ice, and delivered immediately to the laboratory. Fruit samples of each cultivar were divided into three maturity categories of immature, midripe, and ripe on the basis of skin color. For the immature category, the entire fruit had green skin in both cultivars. For the midripe category, the fruit was approximately 50% red and yellow skin in both cultivars. For the ripe category, Super Spur skin was completely red, and Yellow Gem skin was uniformly yellow.

Chemical Analysis. The nonvolatile acid and sugar contents were determined from 75% ethanol extracts of whole fruit for each maturity stage as previously described (Chapman and Horvat, 1989; Chapman et al., 1991a). Total pectin content was determined according to the method of Blumenkrantz and Asboe-Hansen (1973) after extraction as previously described (Chapman and Horvat, 1990). Pectin carbohydrate composition was determined by capillary GLC after hydrolysis with pectinase from *Aspergillus niger* (Sigma Chemical Co.) (Chapman and Horvat, 1990). The procedure was modified by immersing the tubes into boiling water for 2 min to stop enzymatic activity. The tubes were cooled, and the solution was adjusted to approximately pH 1.0 (pHydrion paper) with two drops of 1.0 M HCl. Oxime TMS derivatives were made after drying (Chapman and Horvat, 1989).

RESULTS AND DISCUSSION

The changes in nonvolatile acids and sugars during maturation of mayhaw fruit are shown in Figures 1–4. Values shown in the figures are the average of two sample extractions, TMS derivatives, and subsequent GLC analysis. Malic acid levels declined more rapidly in Super Spur than in Yellow Gem during maturation. This fact may account for the higher levels of this acid found in the ripe fruit of Yellow Gem and other mayhaw cultivars in *C. aestivalis* than are found in *C. rufula* and *C. opaca*. However, one exception has been noted in the cultivar T.

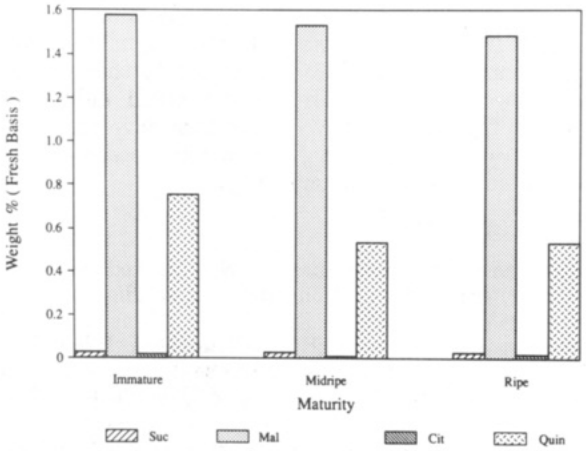

Figure 1. Changes in nonvolatile acids of Yellow Gem mayhaw fruit at three maturity stages. Suc, succinic; Mal, malic; Cit, citric; Quin, quinic.

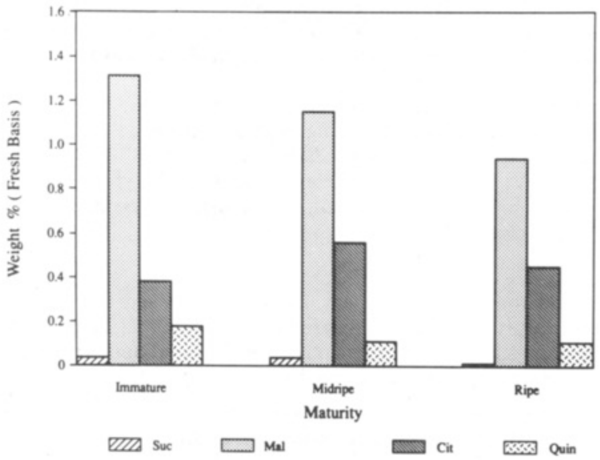

Figure 2. Changes in nonvolatile acids of Super Spur mayhaw fruit at three maturity stages. Suc, succinic; Mal, malic; Cit, citric; Quin, quinic.

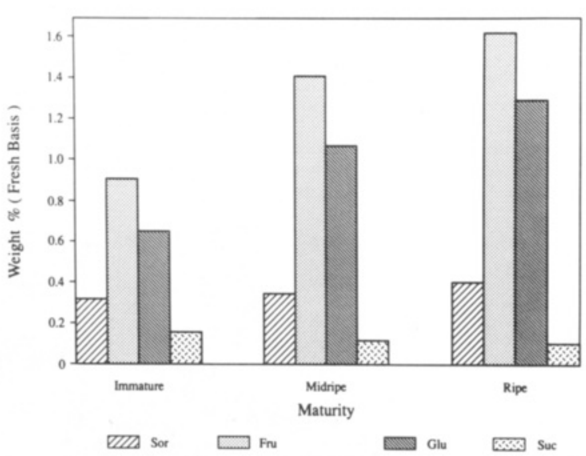

Figure 3. Changes in sugars of Yellow Gem mayhaw fruit at three maturity stages. Sor, sorbitol; Fru, fructose; Glu, glucose; Suc, sucrose.

O. Superberry (*C. opaca*), which had the highest malic acid levels of all cultivars analyzed (Chapman et al., 1991a). Citric acid was the second most abundant nonvolatile acid found in Super Spur and showed an increase at the midripe stage followed by a decrease at the ripe stage. However, citric acid was never the major acid at this stage of development as was observed at about 30 days prior to physiological maturity in peaches (Chapman and Horvat, 1990; Chapman et al., 1991b). Yet the trends of citric acid in Super Spur were similar to those found in peaches.

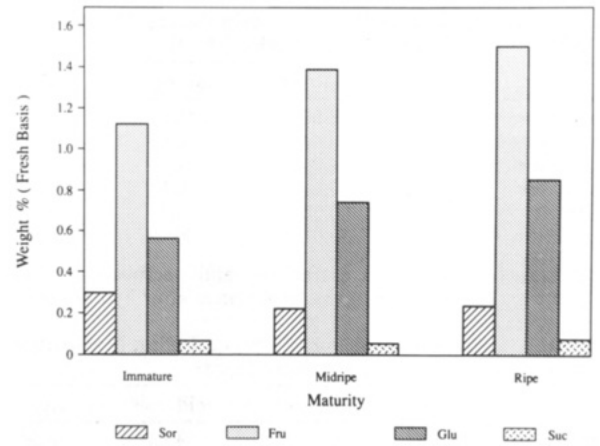

Figure 4. Changes in sugars of Super Spur mayhaw fruit at three maturity stages. Sor, sorbitol; Fru, fructose; Glu, glucose; Suc, sucrose.

Super Spur had much higher citric acid levels at the ripe stage, while this acid was found in only trace amounts in Yellow Gem (Figures 1 and 2). Quinic acid levels also decreased in both cultivars with maturity, but the levels were much higher in Yellow Gem in Super Spur (Figures 1 and 2). The high levels of quinic acid during maturation of Yellow Gem may be typical of *C. aestivalis*, since two unnamed cultivars of this species also had higher quinic acid levels in ripe fruit than are found in other cultivars (Chapman et al., 1991a). The levels of succinic acid were ≤0.05% in both cultivars and could be considered trace amounts.

Changes in sugars were similar in both cultivars with fructose and glucose increasing with maturity, while sucrose and the sugar alcohol, sorbitol, changed very little (Figures 3 and 4). Fructose was the principal sugar during maturation in both cultivars and was the major surgar in 10 cultivars representing 3 species of mayhaw fruits (Chapman et al., 1991a). The level of glucose increased at a greater rate in Yellow Gem than it did in Super Spur. Therefore, the higher glucose levels may be a trait of *C. aestivalis*, since these levels were much less in the ripe fruit of *C. opaca* and *C. rufula* (Chapman et al., 1991a).

Total pectin levels based on fresh weight changed very little in either cultivar during maturation. In Super Spur, pectin amounts were 0.43% at the immature stage and 0.45% at the ripe stage. Levels were slightly higher in Yellow Gem, ranging from 0.65% in the immature fruit to 0.73% in ripe fruit. The total amount of pectin per fruit would be expected to increase since fruit fresh weight would have increased.

Generally, only about 27% of pectin can be hydrolyzed to free sugars with pectinase under reaction conditions described previously (Chapman and Horvat, 1990); however, adjusting the mixture to pH 1.0 after the enzymatic reaction typically increased free sugar yields to 60–80% (unpublished data). This possibly could be due to the release of bound sugars from pectin under acidic conditions. Pectin solutions (pH 1.0) at zero reaction time yielded only traces of free arabinose and glucose. Therefore, the higher yields of hydrolyzed sugars may represent a more realistic carbohydrate composition of mayhaw pectin.

Tables I and II show the changes in carbohydrate composition of mayhaw pectin during fruit maturation. The percentage of arabinose in pectin declined appreciably while the percentage of galacturonic acid increased in both cultivars. These trends were similar to carbohydrate compositional changes in pectin during peach maturation,

Table I. Sugar Composition of Pectin during Maturation of Yellow Gem (*C. aestivalis*) Mayhaw Fruit[a]

sugar	immature[b]	midripe[b]	ripe[b]
arabinose	18.51	12.65	7.29
rhamnose	0.44	0.56	0.55
galactose	4.90	4.96	5.12
mannose	0.51	0.64	0.73
glucose	0.62	1.16	1.08
galacturonic acid	75.01	80.02	85.22

[a] Average of two pectin extractions and pectinase reactions. [b] Percent individual sugar to the total sugars after hydrolysis.

Table II. Sugar Composition of Pectin during Maturation of Super Spur (*C. opaca*) Mayhaw Fruit[a]

sugar	immature[b]	midripe[b]	ripe[b]
arabinose	12.11	4.89	5.24
rhamnose	0.48	0.51	0.44
galactose	5.62	5.93	5.30
mannose	0.52	0.58	0.55
glucose	0.65	0.91	0.60
galacturonic acid	80.61	87.42	87.87

[a] Average of two pectin extractions and pectinase reactions. [b] Percent individual sugar to the total sugars after hydrolysis.

although the pectin carbohydrate composition in ripe fruit was different between mayhaws and peaches (Chapman and Horvat, 1990). The carbohydrate composition in Super Spur pectin changed very little from the midripe to ripe stages of maturity. In contrast, the composition continued to change through all three stages in Yellow Gem pectin. Galactose was also a major component of mayhaw pectin in both cultivars, but the percentage of this sugar changed very little with fruit maturity. Mannose and glucose were shown to increase appreciably with maturation in Yellow Gem, a trend not observed in Super Spur. Rhamnose was a minor sugar found in mayhaw pectins.

Results of this study show that chemical compositional changes were different between the two mayhaw cultivars during maturation and may be related to their genetic diversity. Therefore, such changes could aid in the selection of certain mayhaw cultivars for development of new and improved hybrids, which may possess unique chemical compositions at maturity.

LITERATURE CITED

Blumenkrantz, N.; Asboe-Hansen, G. New Method for Quantitative Determination of Uronic Acids. *Anal. Biochem.* **1973**, *54*, 484–489.

Champman, G. W., Jr.; Horvat, R. J. Determination of Nonvolatile Acids and Sugars from Fruits and Sweet Potato Extracts by Capillary GLC and GLC/MS. *J. Agric. Food Chem.* **1989**, *37*, 947–950.

Chapman, G. W., Jr.; Horvat, R. J. Changes in Nonvolatile Acids, Sugars, Pectin, and Sugar Composition of Pectin During Peach (Cv. Monroe) Maturation. *J. Agric. Food Chem.* **1990**, *38*, 383–387.

Chapman, G. W., Jr.; Horvat, R. J.; Payne, J. A. The Nonvolatile Acid and Sugar Composition of Mayhaw Fruits (*Crataegus aestivalis, C. opaca, C. rufula*). *J. Food Qual.* **1991a**, *14*, 435–439.

Chapman, G. W., Jr.; Horvat, R. J.; Forbus, W. R., Jr. Physical and Chemical Changes During the Maturation of Peaches (Cv. Majestic). *J. Agric. Food Chem.* **1991b**, *39*, 867–870.

Payne, J. A.; Krewer, G. W.; Eitenmiller, R. R. Mayhaws: Trees of pomological and ornamental interest. *Hortscience* **1990**, *25*, 245–246, 375.

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