Carbohydrate and Acid Contents of Gala Apples and Bartlett Pears from Regular and Controlled Atmosphere Storage

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Gala apples and Bartlett pears were harvested over two crop seasons at different maturities and growing sources then stored in refrigerated storage alone and in controlled atmosphere storage (1% O_2 plus 1% CO_2 or 2% O_2 plus 3% CO_2). Before and after storage of 45 or 90 days, the juice from the fruit was examined for carbohydrate and acid compositions and contents. For Gala apples, the type and length of storage had no significant effect on juice carbohydrate and acid contents and compositions, whereas the time of harvest greatly influenced both parameters. Storage atmosphere did not affect the carbohydrate and acid contents and compositions of Bartlett pear juice; however, the source of the fruit and subsequent amount of ripening did appear to significantly cause changes in the same parameters. The carbohydrate and acid compositions and contents of Gala apple juice were within the compositional range for worldwide apple juice. Bartlett pear juice contained significantly greater concentrations of citric acid than shown in previously published studies.

Keywords: Sucrose; glucose; fructose; sorbitol; quinic; malic; skikimic; citric; fumaric

INTRODUCTION

Gala is an apple cultivar growing in popularity and volume in Washington State, with ~2680 ha in production (Washington Agriculture Statistics Service, 1993), and this volume is predicted to steadily increase. The storage-life of Gala apples in regular storage (RA) is relatively short (Drake, 1991). Particular attention has been given to the storage of Gala apples in controlled atmosphere (CA) to lengthen storage life. Because Gala apples are harvested in early August, storage facilities cannot be filled with Gala apples alone; thus, CA storage of Gala apples with other cultivars or species is desirable. Washington-grown Bartlett pears also mature during early August and have a storage life similar to that of Gala apples (Drake and Eisele, 1997). Bartlett pears can be certified from CA only after 45 days in storage (Washington Agriculture Code, 1989), a length of storage that would also meet the CA certification for Gala apples (Washington Agriculture Code, 1994). Bartlett pears are a major source of fruit for juice concentrate. Because Gala apple production is increasing in volume and the storage of Gala apples with Bartlett pears is desirable, there is a need for Washington juice processors to expand their knowledge of the carbohydrate and acid contents of these cultivars and any subsequent changes that may occur in storage. Therefore, this study was initiated to determine the carbohydrate and acid contents and compositions of Gala apples and Bartlett pears at different maturities and from different growing sources prior to and after various RA and CA storage times.

Apple juice is the largest volume of juice sold in the United States. The chemical composition of apple juices can vary, and this variation depends on the cultivar, region of production, maturity, and various other hor-

ticultural practices (Leonard and Mayer, 1983). Other researchers (Lee and Wrolstad, 1988) reported that no differences in chemical composition (carbohydrates, acids) could be attributed to a growing region of production. Babsky et al. (1989) determined that no change was evident in sugar or acid content of apple juice concentrate during nonrefrigerated shipment of 55 days. In an earlier paper (Babsky et al., 1983), it was determined that there was a decrease in the titratable acidity and changes in sucrose of apple juice concentrate stored at 37 °C. Kubo and Tamuro (1979) reported a decrease in sorbitol content in apples during cold storage. Lee and Wrolstad (1988) also found a decrease in sorbitol content of apples during storage. Gorin (1973) reported loss of sucrose in Golden Delicious apples during storage. Wrolstad (1985) suggested that the acid content of fruit juice changes during storage. Much information is available on the carbohydrate and acid contents of apples and apple juice. Little information is available on the carbohydrate and acid contents of Gala apples or Bartlett pears.

MATERIALS AND METHODS

This study was conducted over two crop seasons using Royal Gala apples and Bartlett pears. Apples were from a commercial orchard located at Vantage, WA. Apple maturity at each harvest was based on background color (harvest 1, green; harvest 2, white; harvest 3, yellow). Nine hundred apples of uniform size and color were obtained at each harvest, 300 from each of three locations within the orchard. After each harvest the three groups of apples were divided into five random lots of 60 apples each. At the time of each apple harvest, freshly harvested Bartlett pears (900) were obtained from three commercial warehouses located in the vicinity of Wenatchee, WA. Pears were also divided into five random lots of 60 pears each.

Immediately after returning to the laboratory, the apples and pears were placed in storage. One lot of each, apples and pears, was placed in RA storage, and the other four groups

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were placed in CA at 1% O_2 plus 1% CO_2 or 2% O_2 plus 3%CO₂. Apples alone or in combination with pears for both types of storage (RA and CA) were held at 1 °C. Atmospheres were established and maintained with a computer-controlled system (Technical Consulting Services, Chelan, WA). Apples were stored for 45 or 90 days, and pears were stored for 90 days.

Before and after storage, composites of 10 fruit from each combination (cultivar, storage, and replication) were used for analysis. Apples and pears from RA and CA were juiced within 24 h of harvest or 4 h after removal from storage. After juicing, a 5 mL aliquot of the same was frozen prior to analysis. When a sufficient number of samples had been collected, carbohydrate and acid analyses were conducted. Analysis of variance was determined by MSAT-C (1989) using harvest or source as the main plot and storage type and duration as the subplots. On the basis of significant *F* tests, means were separated by Tukey's test ($P \leq 0.05$).

Juice samples were first filtered through a 0.45 μ m membrane. A small part of the volume was used for sugar analysis; the remainder was used for acid analysis after 5.0 mL of juice had been passed through an activated C₁₈ Sep-Pak cartridge (Waters Associates, Milford, MA) as described by Hong and Wrolstad (1986). Degrees Brix values were measured on all samples prior to HPLC analysis using a tabletop Model RFM autorefractometer (Bellingham & Stanley Limited). All carbohydrate and acid compositional data shown in Tables 1–4 were normalized to 11.5 °Brix for apple juice or 12.0 °Brix for pear juice to match the FDA definition for 100% juice. Carbohydrate composition, and organic acids were expressed as milligrams per 100 mL.

For carbohydrate analysis, the HPLC system consisted of a Waters 510 pump, a Waters 710B Wisp autosampler, a Bio-Rad column heater set at 80 °C, and a Bio-Rad refractive index monitor. For acids, the HPLC system consisted of the same type pump and autosampler with a Waters 490 programmable, multiwavelength detector set at 214 nm wavelength. Both HPLC systems were interfaced to a Nelson 760 series data buffer and an IBM XT using a Nelson 3000 series chromatography data system software program (Cupertino, CA). An Aminex HPX-87C monosaccharide analysis column, fitted with a Carbo-C microguard column (Bio-Rad Laboratories, Richmond, CA), was used for carbohydrate analysis. Two Alltech Spherisorb ODS columns in series, ODS-2 followed by ODS-1 fitted with an Alltech direct connect analytical guard column (Alltech Associates, Deerfield, IL), was used for acid analysis. The mobile phase for carbohydrates was 0.01% reagent grade calcium chloride prepared with deionized water, and the flow rate was 0.8 mL/min. The mobile phase for acids was a 0.05 M potassium phosphate buffer adjusted to pH 2.4 with reagent grade phosphoric acid with the same flow rate as for carbohydrates. Carbohydrate standards were prepared by adding 2.00 g each of reagent grade glucose, sucrose, fructose, and sorbitol to a 100 mL volummetric flask and diluting to volume with deionized water. Organic acid standards were prepared by adding 100 mg of reagent grade quinic acid, malic acid, and critic acid plus 10 mg each of reagent grade shikimic acid and fumaric acid to a 100 mL volummetric flask and diluting to volume with deionized water. Injection volumes for standards and samples were 10 μ L.

RESULTS AND DISCUSSION

Harvest maturity had a strong influence on the carbohydrate and acid contents of Gala apples (Table 1). As time of harvest progressed, °Brix values and sucrose and sorbitol contents decreased. The decrease in °Brix values was more evident at the last harvest (harvest 3) compared to the two earlier harvests. Decrease in sucrose content occurred between the first and second harvests, a period of only 7 days. Sorbitol increased between the first and second harvests and then decreased between the second and third harvests. Other studies (Kubo and Tamuor, 1977; Lee and Wrol-

 Table 1. Carbohydrate and Acid Contents of Gala Apples

 from Three Harvests over a 14 Day Time Period^a

Carbohydrates (%)									
harvest	total °Brix (%)) sucrose	e glucose	fructose	sorbitol				
1	11.1a	35.1a	7.9a	54.1a	2.8b				
2	11.8a	34.1b	9.0a	52.9a	3.9a				
3	8.7b	33.7b	8.3a	56.0a	2.0c				
Acids (mg/100 mL)									
harvest	quinic i	malic s	shikimic	citric	fumaric				
1	36.3c 5	71.7a	1.3b	7.9a	0.09b				
2	40.6a 5	61.5a	1.3b	11.4a	0.13a				
3	39.0b 4	84.1b	1.5a	44.8a	0.05c				

^{*a*} Means in a column within analysis (carbohydrates and acids) not followed by a common letter are significantly different ($P \le 0.05$).

Table 2. Carbohydrate and Acid Contents of BartlettPears at Harvest from Three Sources in the Wenatchee,WA, Growing District a

Carbohydrates (%)								
source	total °Brix (%	5) sucr	ose	glucose	fructose	sorbitol		
1	8.4b	5.0a		11.3c	64.0a	19.6b		
2	11.2a	3.7	a	12.9b	60.3c	23.1a		
3	9.1b	3.6	а	14.0a	62.5b	19.8b		
Acids (mg/100 mL)								
source	quinic	malic	sh	ikimic	citric	fumaric		
1		64.6b		4.4b	305.9b	0.03b		
2		98.1a		3.8b	363.6a	0.16a		
3	48.4a 1	98.3a	(6.7a	319.3b	0.15a		

^{*a*} Means in a column within analysis (carbohydrates and acids) not followed by a common letter are significantly different ($P \le 0.05$).

stad, 1988) suggest that sorbitol decreases over time in other apple cultivars, and this increase followed by a decrease, in this study, should not be expected.

No differences were observed in glucose or fructose contents in Gala apples in relation to time of harvest (Table 1). Malic and fumaric acid contents of Gala apples decreased as time of harvest progressed. This decrease in acid content was dramatic for both malic acid (15%) and fumaric acid (44%). There was no change in citric acid, but there was an increase in quinic (7%) and shikimic (16%) as harvest progressed over the 14 day period. The highest fumaric and quinic acid contents for apples was at harvest 2, with a decrease for both acids at harvest 3.

The source of the fruit had a major influence on the carbohydrate and acid contents of Bartlett pears (Table 2). Although all of the pears, in this study, were grown in the Wenatchee, WA, growing district, differences in glucose and fructose were present in pears from all three sources as were differences in °Brix values and sorbitol from two sources. °Brix values of pears were similar from two sources, but the glucose and fructose contents of the pears were different. Pears with the highest °Brix values (11.2) had low fructose values, high sorbitol values, and intermediate glucose values. These differences suggest that many environmental factors can influence the individual carbohydrate production and composition of Bartlett pears.

Source also had a major influence on the individual acids determined for Bartlett pears at harvest (Table 2). Malic acid varied from 164.6 mg/100 mL from source 1 fruit to 198.3 mg/100 mL from source 3 fruit. Citric

 Table 3. Carbohydrate and Acid Contents of Gala Apples

 after 45 and 90 Days of Regular or Controlled

 Atmosphere Storage^a

Carbohydrates (%)								
atmos- phere ^b	days in storage	total °Brix (%)	sucrose	glucose	fructose	sorbitol		
RA	45	11.7a	31.8a	11.2c	54.7b	2.3b		
	90	11.2b	27.0c	14.5a	55.9a	2.6a		
CA	45	11.6a	26.0d	12.8b	54.0b	2.2b		
	90	11.3ab	28.7b	17.8a	54.0b	2.6a		
		Acid	s (mg/100) mL)				
atmos- phere	days in storage	quinic	malic	shikimic	citric	fumaric		
RA	45	32.6b	465.9b	1.3ab	9.6b	0.08a		
	90	35.8a	453.5b	1.4a	13.2a	0.12a		
CA	45	35.3a	498.8a	1.4a	9.8b	0.11a		
	90	31.6b	473.1b	1.2b	8.5b	0.11a		

^{*a*} Means in a column, within sugars or acids, not followed by a common letter are significantly different ($P \le 0.05$). ^{*b*} RA, regular atmosphere storage (1 °C); CA, controlled atmosphere storage (1% O₂ and 1% CO₂ at 1 °C).

acid, the major acid in Bartlett pear juice, varied from 305.6 mg/100 mL in source 1 fruit to 363.6 mg/100 mL in source 2 fruit.

Time in RA storage had a major influence on the °Brix values and sucrose, glucose, fructose, and sorbitol contents of Gala apples (Table 3). Brix values and sucrose decreased as time in RA storage increased from 45 to 90 days. Glucose, fructose, and sorbitol increased in RA storage between 45 and 90 days. Gala apples in CA storage for a similar time displayed increased sucrose, glucose, and sorbitol, but °Brix values and fructose contents remained constant. °Brix content of Gala apples in CA declined at a slower rate than that of similar apples in RA. Sucrose content of apples decreased in RA over time but increased in CA storage. Glucose content increased in apples from both RA and CA during storage, but the increase in glucose was more apparent in apples from RA. Fructose contents increased with time for all apples in RA, but no change was apparent for apples in CA during the same time period. Sorbitol content increased during storage, for apples in RA and CA storage, but this increase was more apparent for apples in CA.

Quinic acid increased in apples stored in RA and decreased in apples stored in CA. There was a decrease in malic acid in apples from CA storage, but malic acid content remained constant in apples in RA storage. Skikimic acid remained the same for apples in RA but decreased during CA storage. Citric acid increased dramatically for apples in RA storage, but this change was not apparent for apples in CA. No change in fumaric acid was apparent regardless of storage type.

Storage atmosphere had no influence on the individual carbohydrate content of Bartlett pears (Table 4), but a storage atmosphere of $2\% O_2$ and $1\% CO_2$ resulted in pears with a lower °Brix content than pears in $1\% O_2$ and $3\% CO_2$. When Bartlett pears were ripened after CA storage, there were changes in individual carbohydrates but not in total °Brix values. Sucrose content of pears increased during 5 days of ripening regardless of the source of the pears. Depending on the source, there was an increase or decrease in the amount of glucose present. In two of the three sources there was an increase in glucose, but pears from one source lost glucose during ripening. Fructose content remained

Table 4. Carbohydrate and Acid Contents of BartlettPears after 90 Days of Controlled Atmosphere (TwoDifferent Atmospheres) and the Interaction of Sources ofPears and Ripening Time^a

		Total Ca	rbohydra	tes (%)		
		total				
atmospher	е	°Brix (%)	sucrose	glucose	fructose	sorbitol
1% O ₂ and 1% CO ₂		9.6b	3.3a	18.7a	61.7a	16.3a
2% O ₂ and 3% CO ₂		10.1a	3.2a	18.6a	91.9a	16.3a
source \times rip	ening ti	me (days)				
1	0	9.0c	1.6cd	19.9ab	61.0b	17.5b
	5	9.2bc	5.4a	17.1c	66.3a	11.2d
2	0	10.6a	1.3d	17.1c	61.5b	20.2a
	5	10.9a	4.0b	19.3ab	61.0b	15.8b
3	0	10.2ab	2.6c	18.0bc	61.7b	17.7b
	5	9.3bc	4.6ab	20.6a	59.5b	15.3c
		Acids	(mg/100 i	mL)		
atmospher	re	quinic	malic	shikimic	citric	fumaric
1% O ₂ and 1	% CO ₂	52.0a	110.1a	3.9a	273.1a	0.23a
2% O2 and 3	$\% CO_2$	47.7a	113.0a	3.6b	277a	0.22a
source \times rip	ening ti	me (days)				
1	ŏ	46.7ab	144.4a	4.5b	348.2a	0.29a
	5	40.4b	65.7c	2.2d	247.1cd	0.26ab
2	0	44.8ab	146.4a	3.1c	308.4b	0.22b
	5	55.4ab	99.3b	2.2d	235.3d	0.25ab
3	0	61.6a	144.2a	6.2a	272.5c	0.13c
	5	50.2ab	69.0c	4.3b	238.7cd	0.21b

 a Means in a column, within atmosphere or source \times ripening time, not followed by a common letter are significantly different (P \leq 0.05).

constant during ripening in two of the three sources but dramatically increased in one source during ripening. Sorbitol content decreased in pears, during ripening, regardless of the source. These results differ from a limited fruit ripening study in which Wrolstad et al. (1989) illustrated that ripening had no effect on the sorbitol content of Bartlett pear juice.

Storage atmosphere had no influence on the quinic, malic citric, or fumaric acid content of Bartlett pears (Table 4). Shikimic acid was higher in Bartlett pears stored in $2\% O_2$ and $3\% CO_2$ than in pears stored in 1%O₂ and 1% CO₂. Five days of ripening after CA storage resulted in changes in the contents of malic, shikimic, citric, and fumaric acid, but no change in quinic acid content occurred. Malic and shikimic acid decreased during 5 days of ripening regardless of the source of the pears. Citric acid decreased during ripening in two of the three sources of pears but increased in one source during ripening. Fumaric acid contents were similar after ripening in two of the three sources but increased in one source of pears. In this study, citric acid was the prominent organic acid present in pear juice. In an earlier study (Wrolstad et al., 1989), malic acid was the prominent organic acid in Bartlett pear juice, with citric acid being secondary in concentration.

When comparing carbohydrate and acid compositions of Gala apples to Bartlett pears, the apples were much lower in sorbitol and citric acid and higher in sucrose and malic acid than the pears. Other carbohydrates and acids tended to vary somewhat between the two fruits but were within the same compositional magnitudes.

CONCLUSIONS

Type of storage (RA or CA) did not significantly influence the °Brix content of Gala apples. However, the type of storage did display an influence on individual carbohydrate content, particularly sucrose. Type of storage displayed little or no influence on the acid content of Gala apples. Within the short storage period (90 days) of this study, Gala apples from either RA or CA would be similar in carbohydrate and acid contents.

Time of harvest had a significant influence on the carbohydrate and acid contents of Gala apples. In this study, care was taken to ensure that maturities were similar between harvests, but time on the tree had a major influence on the final carbohydrate and acid contents of the apple. Compared to a publication by Elkins et al. (1996) on the characterization of 92 commercially produced apple juice concentrates collected over a three year period from the major processing regions of the world, the organic acid and carbohydrate compositions of Gala apple juice in this study falls within the three year minimum and maximum range data summary for the study.

The °Brix content of Bartlett pears were higher when the fruit was stored in a 2% O_2 and 3% CO_2 atmosphere rather than in a 1% O_2 and 1% CO_2 atmosphere, but no other carbohydrate or acid differences were noted as a result of storage in different atmospheres. After CA storage of the Bartlett pears, the source of the fruit and the subsequent amount of ripening appear to be responsible for the major changes in carbohydrate and acid contents and compositions.

There is very little published information on the composition of worldwide pear juice composition. The sucrose and citric acid compositions of the Bartlett pear juice in this study (Tables 2 and 4) would not meet the present German RSK Values, Guidelines and Tolerance for specified constituents in pear juice (Wallrauch and Faethe, 1988). The current RSK lists the citric acid range as 10–200 mg/100 mL for pear juice. Although all of the fruit samples in this study were authentic, every juice sample exhibited a citric acid content >200 mg/100 mL.

LITERATURE CITED

- Babsky, N. E.; Toribio, J. L.; Lozana, J. E. Influence of storage on the composition of clarified apple juice concentrate. *J. Food Sci.* **1986**, *51*, 564–567.
- Babsky, N. E.; Wrolstad, R. E.; Durst, R. W. Influence of commercial shipping on the color and composition of apple juice concentrate. *J. Food Qual.* **1989**, *12*, 355–367.
- Drake, S. R. Storage regimes for apples. *Proc. Wash. Tree Fruit Postharvest Conf.* **1991**, *7*, 63–64.

- Drake, S. R.; Eisele, T. A. Quality of 'Gala' apples as influenced by harvest maturity, storage atmosphere and concomitant storage with 'Bartlett' pears. *J. Food Qual.* **1997**, *20*, 41– 51.
- Elkins, E. R.; Matthys, A.; Lyon, R.; Huang, C. J. Characterization of Commercially Produced Apple Juice Concentrate. *J. Food Compos. Anal.* **1996**, *9*, 43–56.
- Gorin, N. Several compounds in golden delicious apples as possible parameters for acceptability. *J. Agric. Food Chem.* **1973**, *21*, 670–672.
- Hong, V.; Wrolstad, R. E. Cranberry juice composition. J. Assoc. Off. Anal. Chem. 1986, 69, 594-597.
- Kubo, N.; Tamura, T. *Rep. Natl. Food Res. Inst.* **1979**, *34*, 54–60.
- Kulp, K.; Loreny, K.; Stone, M. Functionality of carbohydrate ingredients in bakery products. *Food Technol.* **1991**, *45*, 137–142.
- Lee, J. S.; Wrolstad, R. E. Apple juice composition: Sugar, nonvolatile acid and phenolic profiles. J. Assoc. Off. Anal. Chem. 1988, 71, 789–794.
- Leonard, R. M.; Mayer, J. C. Fruit and fruit products. *J. Assoc. Off. Anal. Chem.* **1983**, *66*, 1251–1255.
- Wallrauch, W.; Faethe, W. Germany: RSK Values, Guidelines and Tolerances for Specified Constituents in Fruit Juice. In Adulteration of Fruit Juice Beverages; Nagy, S., Attaway, J. A., Rhodes, M. A., Eds.; Dekker: New York, 1988; pp 405– 470.
- Washington Agriculture Code. 16-690-100, Fruit storage; Washington Department of Agriculture: Olympia, WA, 1989; pp 1–3.
- *Washington Argriculture Code.* 15-20-060, Controlled atmosphere storage of fruits and vegetables; Washington Department of Agriculture: Olympia, WA, 1994; pp 1–7.
- Washington Agriculture Statistics Service. *Washington Fruit Survey*, Olympia, WA, 1993.
- Wrolstad, R. E. Chemistry of apple juice, contaminants and adulterations. *Fluess. Obst* **1985**, *52*, 331–332.
- Wrolstad, R. E.; Heatherbell, D. A.; Spanos, G. A.; Durst, R. W.; Hsu, J.; Yorgey, B. M. Processing and Storage Influences on the Chemical Composition and Quality of Apple, Pear, and Grape Juice Concentrates. In *Quality Factors of Fruits and Vegetables*, Jen, J. J., Ed.; American Chemical Society: Washington, DC, 1989; pp 270–292.

Received for review November 16, 1998. Revised manuscript received June 15, 1999. Accepted June 15, 1999. We express appreciation to the Washington State Tree Fruit Research Commission for its financial support of this project.

JF981228X