

# Characterization and the Effect of Maturity at Harvest on the Phenolic and Carotenoid Content of Northeast USA Apricot (*Prunus armeniaca*) Varieties

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**ABSTRACT:** The phenolic and carotenoid content and quality indices of five Northeast apricot varieties were assessed over two years and the impact of maturity at harvest was evaluated. Four varieties were analyzed at commercial and tree ripe stages and one variety after storage for 4 weeks (0–1 °C, 90–95% relative humidity). Total phenolic content ranged from 44.0 to 345.1 mg/100 g, total antioxidant capacity (oxygen radical absorbance capacity assay) from 2096.9 to 7165.1  $\mu\text{mol}/100\text{ g}$ , and total carotenoid content from 1312.1 to 7371.1  $\mu\text{g}/100$ , fresh weight. ‘Hargrand’ apricot had the highest phenolic and carotenoid content. Catechin, chlorogenic acid, and neochlorogenic acid were the predominant phenolic compounds and  $\beta$ -carotene was the predominant carotenoid compound. Carotenoid content increased with ripening and postharvest storage while changes in phenolic content and antioxidant capacity were variety-dependent. Results show the apricot varieties studied to be good or excellent sources of vitamin A despite moderate carotenoid content attributed to cultivation in a colder climate.

**KEYWORDS:** *Prunus armeniaca*, apricot, phenolic, carotenoid, antioxidant, maturity, ripening

## INTRODUCTION

Consumption of fruits has been encouraged because of the myriad health benefits they offer.<sup>1,2</sup> Phenolic and carotenoid compounds are widely distributed in plant tissue and involved in a range of functions including fruit color and taste. In the apricot, *Prunus armeniaca*, the main phenolic compounds identified include flavan-3-ols (catechin, epicatechin), hydroxycinnamic acids (neochlorogenic acid, chlorogenic acid), flavonol glycosides (rutin, quercetin-3-glucoside and other quercetin derivatives) and anthocyanins (cyanidin-3-glucoside).<sup>3–5</sup> Carotenoids include carotenes ( $\alpha$ -,  $\beta$ - and  $\gamma$ -carotene) and xanthophylls (lutein, zeaxanthin, violaxanthin and  $\beta$ -cryptoxanthin).<sup>6–8</sup>

These phytochemicals have been found to have positive impacts on human health. Antioxidants, comprising both phenolic and carotenoid compounds, have been linked to a reduction in the incidence of cardiovascular diseases and some cancers while carotenoids play an essential role in vision.<sup>9,10</sup> Chlorogenic and neochlorogenic acids have been found to be chemopreventive toward breast cancer.<sup>11</sup>  $\beta$ -carotene,  $\alpha$ -carotene and  $\beta$ -cryptoxanthin are vitamin A precursors while zeaxanthin and lutein, although lacking provitamin A properties, accumulate in the macular tissue of the eye and protect against age-related macular degeneration.<sup>10,12</sup> Additionally,  $\beta$ -carotene has been suggested to have a preventive effect against lung and colorectal cancer<sup>13</sup> and lycopene has been linked to a reduced risk of cancer and heart disease.<sup>14</sup> Apricot phytochemical composition and concentration are influenced by a number of factors, including variety, maturity, climate, as well as the part of fruit (peel or flesh) analyzed, with fruit peel containing relatively higher concentrations of phenolic and carotenoid compounds.<sup>3,4,6,7,15</sup>

Apricots are climacteric fruit and may ripen either on- or off-tree. Time of harvest is therefore largely dictated by the intended market and/or purpose of fruit, with produce intended for far-off markets or extended storage harvested earlier than those for local market; the latter group is thought to have better eating quality despite its shorter shelf life. The impact of these practices, mainly fruit maturity at harvest, has received some attention. Dragovic-Uzelac et al.<sup>4</sup> reported that phenolic compounds in these stone fruits are predominant in the initial and early ripening stages of development, but decrease with maturity; opposing findings were reported by Hegedus et al.<sup>16</sup> An increase in carotenoid content has also been observed with ripening.<sup>4</sup>  $\beta$ -carotene has been found to be present throughout fruit development while the presence and concentrations of other carotenoids, particularly xanthophylls, alter from carotenogenesis through fruit development and maturity.<sup>7,8</sup>

Apricot production is predominantly based in parts of Europe and the Mediterranean, with most available information derived from varieties produced in these temperate to subtropical climatic regions. In the United States, apricot production is concentrated in California (approximately 80%), Washington and Utah,<sup>17</sup> with the Northeast USA contributing much smaller quantities. Cultivation in this region is challenging due to adverse climatic conditions that, together with this fruit tree’s inherent restrictions to climatic adaptation, limit production.<sup>18,19</sup> Breeding programs have therefore been targeted at improving cold hardiness, late bloom, and pest and

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disease resistance. Research on resultant varieties has focused on physical and other sensory characteristics but little published data is available on the impact of these modifications on bioactive compounds and nutritional value.

This study was therefore designed to breach the knowledge gap regarding the phenolic and carotenoid composition and content of a selection of economically important apricot varieties currently cultivated in the Northeast USA. Five varieties were selected, including four historically found to ensure crop yield in this region due to their cold hardiness and disease resistance.<sup>18,19</sup> The study also included preliminary examination of the effects of seasonal climatic variations and fruit maturity at harvest on these bioactive compounds; a postharvest storage study was carried out for one variety. Physical and chemical characterization was also conducted to provide information on quality indices of these varieties.

## MATERIALS AND METHODS

**Harvest.** Harvests were conducted following the recommendations and practices of local orchards. Five orange-fleshed apricot varieties ('Hargrand', 'Harlayne', 'Harogem', 'Tomcot' and 'Vivagold') were hand-harvested in 2009 and 2010 from the same orchards. While 2009 fruit was harvested according to orchard timelines, in order to further isolate and study pertinent variables suggested by 2009 results, fruit of four varieties was selectively harvested in 2010 at two developmental stages—'commercial ripe' and 'tree ripe'—with the latter occurring on average 8 days after the former. Fruit was selected from both the interior and exterior of canopies to obtain a representative commercial sample. Commercial ripe represented fruit harvested early with adequate firmness to withstand handling, transport and storage conditions; tree ripe represented fruit intended for local market and almost immediate consumption (ready-to-eat). Fruit was considered commercially ripe when it had attained full size and color development yet was still very firm, while tree ripe fruit had decreased firmness and could easily be abscised from the tree. Fruit of one variety ('Hargrand') harvested at commercial ripeness was stored for four weeks at 0–1 °C and 90–95% relative humidity, after which it was analyzed as a third treatment—storage.

**Quality Indices.** Analyses were performed in triplicate, allotting 5 fruit per replicate. Color parameters were measured with a HunterLab UltraScan XE with a 2003 Diffuse/8° Instrument Standard and Light Trap (Hunter Associates Laboratory Inc., Reston, VA) and firmness with a TA-XT2 Texture Analyzer (Texture Technologies Corp., Scarsdale, NY) using a compression test conducted with a 50 mm cylindrical probe. Weight and cross-sectional diameter were also recorded. Soluble solids (Leica Auto ABBE refractometer; Leica Inc., Buffalo, NY), pH (Accumet Basic AB15 pH meter; Fisher Scientific, Waltham, MA) and titratable acidity in malic acid equivalents (Mettler Toledo 20 compact titrator; Mettler-Toledo Inc., Columbus OH) were measured from juice extracted using a food processor. Moisture content values were obtained from the weight differences before and after lyophilization (Magnum Series MX53 freeze-dryer, Millrock Technology, Kingston, NY) to constant weight. Homogenized lyophilized fruit was packaged in moisture-proof bags and stored at 0 °C protected from light until further analyses were conducted.

**Extraction of Phenolic Compounds.** The method described by Kim and Lee<sup>20</sup> was followed. Ten mL methanol/water solution (80:20, v/v) was added to 1 g freeze-dried sample, flushed with nitrogen and sonicated. Samples were then centrifuged at 10 000 rpm for 20 min at 4 °C (Sorvall RC-5B Centrifuge; ThermoScientific, Waltham, MA). Supernatant was decanted into a 25 mL volumetric flask and extraction repeated. Supernatants were combined and topped up to 25 mL with the methanol/water solution.

**Total Phenolic Content Determination.** Procedures by Kim and Lee<sup>20</sup> based on the Singleton and Rossi analysis<sup>21</sup> were employed. Results were expressed as mg gallic acid equivalents (GAE) per 100 g fresh weight (FW).

**Phenolic Compound Analysis.** Qualitative and quantitative phenolic compounds analyses followed methods described by Kim and Padilla-Zakour.<sup>22</sup> An Agilent/Hewlett-Packard series 1100 (Agilent Tech., Palo Alto, CA) was used with a C18 reversed-phase Symmetry Analytical column (250 mm × 4.6 mm, 5 μm; Water Corp. Milford, MA). The thermostat was set at 25 °C and flow rate at 1 mL/min; the diode-array monitored wavelengths 280 (flavan-3-ols), 320 (cinnamic acids), 370 (flavonol glycosides) and 520 nm (anthocyanins). A linear solvent gradient was composed of a binary mobile phase system with solvent A, 0.1% phosphoric acid in HPLC grade water, and solvent B, 0.1% phosphoric acid in HPLC grade acetonitrile. Solvents were applied for 55 min as follows: 92% A/8% B at 0 min, 89% A/11% B at 4 min, 65% A/35% B at 25 min, 40% A/60% B at 30 min, 40% A/60% B at 40 min, 65% A/35% B at 45 min, 89% A/11% B at 50 min, 92% A/8% B at 55 min. Chlorogenic acid, catechin, epicatechin, rutin, cyanidin-3-glucoside and quercetin-3-glucoside were identified using authentic standards (Sigma Aldrich, St. Louis, MO) and remaining compounds tentatively identified using retention time and spectra reported in related literature; cyanidin-3-glucoside and quercetin-3-glucoside standards were available in sufficient quantities for identification but not quantification. Results were reported as mg or mg equivalents (eqv) of available standards/100 g FW. Epigallocatechin and unknowns 1 and 2 reported as catechin eqv, neochlorogenic acid as chlorogenic acid eqv, quercetin-3-glucoside and the quercetin derivative as quercetin eqv and cyanidin-3-glucoside as cyanidin eqv.

**Total Antioxidant Capacity Assay.** The oxygen radical absorbance capacity (ORAC) assay, as described by Huang et al.<sup>23</sup> was used. Aliquots of 25 μL of phenolic extract, blank (75 mM phosphate buffer), and standardized dilutions (0–100 μM) of 6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox; Sigma Aldrich) were pipetted in a preset format into a Costar 96-well black opaque plate (Corning Costar Corporation, Cambridge, MA). A 150 μL aliquot of 0.004 μM sodium fluorescein solution was dispensed into each well and the plate inserted into a BioTek Synergy HT plate reader (BioTek Instruments, Winooski, VT). After a 30-min incubation at 37 °C, 25 μL of 2,2'-Azobis (2-amidinopropane) dihydrochloride (Wako Chemicals, Richmond VA) was dispensed into each well. Fluorescence was measured at 1 min intervals over 1 h at 485 nm excitation wavelength and 528 nm emission wavelength. Results were reported as μmol Trolox equivalents (TE)/100 g FW.

**Carotenoid Compound Analysis.** Modifications to methods by Craft et al.<sup>24</sup> were employed in the extraction, identification and quantification of carotenoids. One gram of freeze-dried sample was homogenized and reconstituted with deionized distilled water then extracted with 20 mL methanol/tetrahydrofuran (50:50, v/v) solution and 10% (w/w) magnesium carbonate. Astaxanthin was included as an internal standard (100 μg/kg) to account for losses occurring during extraction. Extracts were centrifuged at 6000 rpm for 10 min at 4 °C, supernatant recovered and precipitate re-extracted. A saponification step tested during method development was not included as it was found to render zeaxanthin and astaxanthin undetectable.<sup>25,26</sup> Supernatants were combined with 50 mL petroleum ether stabilized with 0.2% butylhydroxytoluene (BHT) and 25 mL 20% sodium chloride solution in a separatory funnel. The petroleum ether fraction was collected and evaporated with a rotary vacuum finishing under nitrogen gas. Aliquots were dissolved in 2 mL ethanol stabilized with 30 ppm BHT. An Agilent series 1100 with a Zorbax XDB-C18 column (150 mm × 4.6 mm, 5 μm; Agilent Tech., Palo Alto, CA) fitted with a guard column of the same packing material was used. The thermostat was set at 23 °C and flow rate at 1 mL/min; the diode-array was set to monitor the wavelengths 450 and 470 nm. A gradient was set up with a binary mobile phase system of solvent A, 0.1% phosphoric acid in HPLC grade water, and solvent B, 0.1% phosphoric acid in HPLC grade acetone. Solvents were applied for 35 min as follows: 30% A/70% B from 0 to 20 min, 0% A/100% B from 20 to 30 min and 70% A/30% B from 30 to 35 min with a 5 min post-run. β-Carotene, β-cryptoxanthin, zeaxanthin, lutein and astaxanthin were identified and quantified using authentic reference samples (Sigma Aldrich). Results were reported in μg/100 g FW. Total carotenoid content was derived

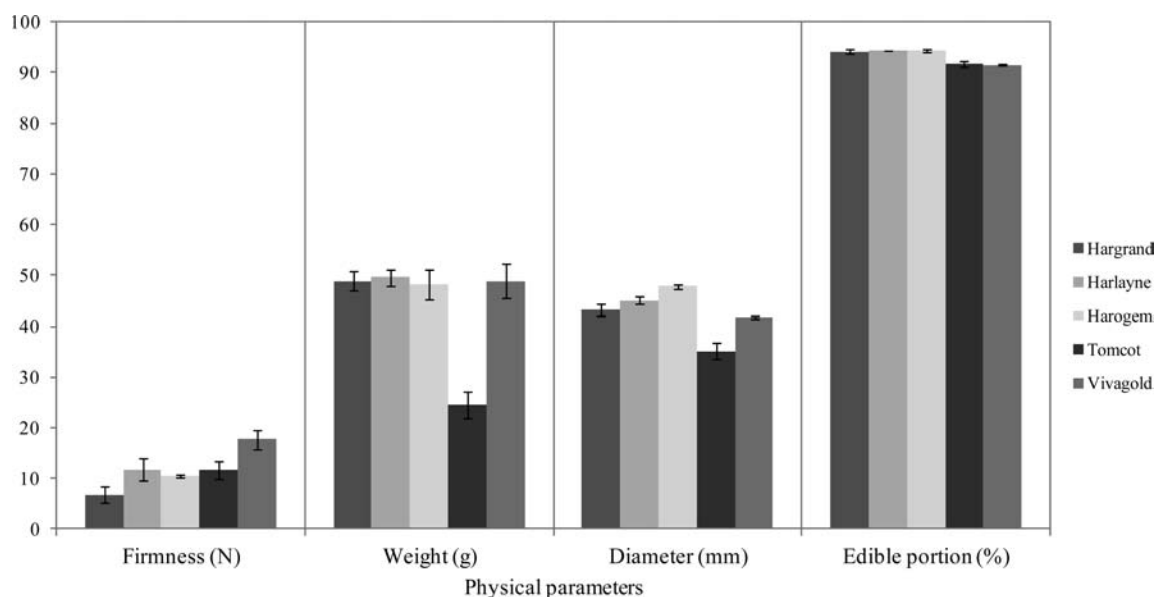


Figure 1. Firmness, weight, cross-sectional diameter and edible portion of Northeast apricot varieties evaluated in 2010 ( $n = 15$ ).

Table 1. Color  $L$ ,  $a$  and  $b$  Values of Flesh and Peel of Northeast Apricot Varieties Evaluated in 2009 and at Commercial Ripe (CR) and Tree Ripe (TR) Stages in 2010 ( $n = 15$ )

variety <sup>a</sup>	part	$L$			$a$			$b$		
		2009	2010		2009	2010		2009	2010	
			CR	TR		CR	TR		CR	TR
Hargrand	flesh	54.6 ± 1.1	46.0 ± 1.1 a	42.8 ± 1.8 b	18.6 ± 1.3	21.6 ± 0.3 a	21.0 ± 0.6 a	38.1 ± 2.4	34.6 ± 0.5 a	31.6 ± 1.7 b
	peel	56.2 ± 0.0	55.4 ± 0.7 a	53.1 ± 1.8 a	20.3 ± 1.6	19.5 ± 0.7 a	20.2 ± 2.3 a	41.9 ± 2.2	35.6 ± 0.1 a	35.4 ± 1.9 a
Harlayne	flesh	61.8 ± 0.5	54.9 ± 4.5 a	51.7 ± 3.5 a	22.7 ± 0.5	24.3 ± 1.1 a	19.6 ± 2.0 b	46.4 ± 0.8	41.7 ± 0.6 a	37.3 ± 3.0 a
	peel	55.0 ± 3.7	52.6 ± 4.9 a	53.4 ± 2.1 a	28.8 ± 3.0	29.3 ± 1.2 a	26.7 ± 0.9 b	40.8 ± 4.1	35.2 ± 7.2 a	39.9 ± 2.2 a
Harogem	flesh	59.9 ± 0.6	57.4 ± 1.9 a	56.2 ± 1.7 a	23.7 ± 0.4	21.9 ± 0.4 a	20.2 ± 1.6 a	45.8 ± 0.3	40.7 ± 1.0 a	40.5 ± 1.2 a
	peel	53.5 ± 4.5	49.7 ± 1.9 a	50.8 ± 0.3 a	31.2 ± 3.3	27.6 ± 0.4 a	28.6 ± 0.9 a	43.1 ± 5.2	31.0 ± 2.0 b	34.4 ± 0.2 a
Tomcot <sup>b</sup>	flesh	61.6 ± 1.3	–	49.3 ± 3.8	23.1 ± 0.3	–	20.1 ± 1.5	43.6 ± 1.0	–	36.6 ± 3.0
	peel	58.1 ± 1.2	–	56.5 ± 3.7	29.1 ± 1.9	–	24.7 ± 0.2	50.0 ± 0.7	–	41.7 ± 3.2
Vivagold	flesh	58.4 ± 1.3	59.9 ± 0.4 a	56.8 ± 0.7 b	23.7 ± 0.9	25.6 ± 1.0 a	26.5 ± 0.4 a	43.7 ± 1.6	44.2 ± 0.8 a	42.9 ± 0.9 a
	peel	61.2 ± 0.5	61.3 ± 1.3 a	58.6 ± 0.7 b	26.4 ± 2.4	28.9 ± 1.2 a	30.7 ± 0.8 a	49.5 ± 1.3	44.0 ± 1.0 a	40.4 ± 0.9 b

<sup>a</sup>Within a variety, means not followed by the same letter indicate a significant difference between 2010 commercial ripe and tree ripe fruit flesh or peel for a color parameter (Tukey test,  $\alpha = 0.05$ ). <sup>b</sup>'Tomcot' was evaluated only at TR in 2010.

Table 2. Firmness, Weight, Cross-sectional Diameter and Edible Portion of Northeast Apricot Varieties Evaluated at Commercial Ripe (CR) and Tree Ripe (TR) stages in 2010 ( $n = 15$ )

variety <sup>a</sup>	firmness (N)		weight (g)		cross-sectional dm (mm)		edible portion (%)	
	CR	TR	CR	TR	CR	TR	CR	TR
Hargrand	18.7 ± 1.6 a	6.7 ± 1.6 b	52.3 ± 3.1 a	48.9 ± 1.8 a	45.5 ± 1.0 a	43.2 ± 1.2 a	94.2 ± 0.2 a	94.2 ± 0.3 a
Harlayne	28.0 ± 8.7 a	11.8 ± 2.1 b	48.9 ± 3.4 a	49.6 ± 1.6 a	46.4 ± 1.4 a	45.1 ± 0.7 a	94.0 ± 0.6 a	94.4 ± 0.0 a
Harogem	26.4 ± 2.1 a	10.5 ± 0.2 b	42.0 ± 3.0 a	48.2 ± 2.8 a	46.6 ± 1.4 a	47.8 ± 0.5 a	93.5 ± 0.4 b	94.3 ± 0.3 a
Tomcot <sup>b</sup>	–	11.6 ± 1.8	–	24.4 ± 2.6	–	35.1 ± 1.6	–	91.8 ± 0.6
Vivagold	40.3 ± 6.3 a	17.7 ± 1.9 b	34.1 ± 2.2 b	48.9 ± 3.4 a	38.8 ± 0.6 b	41.8 ± 0.3 a	87.9 ± 0.1 b	91.5 ± 0.2 a

<sup>a</sup>Within a variety, means not followed by the same letter indicate a significant difference between commercial ripe and tree ripe fruit for a physical parameter (Tukey test,  $\alpha = 0.05$ ). <sup>b</sup>'Tomcot' was evaluated only at TR in 2010.

by the summation of individual compound concentrations expressed in  $\beta$ -carotene equivalents (BCE)/100 g FW.

**Statistical Analysis.** All extraction and assays were conducted in triplicate. Data were analyzed with JMP 9.0 Statistical Software (SAS Institute Inc., Cary, NC) and reported per 100 g FW. Statistical analyses included analysis of variance (ANOVA) at  $p < 0.05$  and  $p < 0.01$  and comparison of means with the Tukey Significant Difference test at 95% confidence interval.

## RESULTS AND DISCUSSION

A selection of varieties was evaluated, originating from the Harrow Research Station ('Hargrand', 'Harlayne' and 'Harogem') and the Vineland Station ('Vivagold') in Ontario, Canada; 'Tomcot' was developed at the Washington State University, Pullman, WA. The first four cold-hardy varieties had previously been studied by horticulturists Lamb and Styles<sup>18</sup> and found to have good size, attractiveness, eating quality and

**Table 3. Soluble Solids, Titratable Acidity, Sugar-to-acid Ratio, pH and Moisture Content of Northeast Apricot Varieties Evaluated in 2009 and at Commercial Ripe (CR) and Tree Ripe (TR) Stages in 2010 ( $n = 15$ )**

variety <sup>a</sup>	soluble solids (%)			titratable acidity (g malic acid/100 g)			sugar-to-acid ratio		
	2010			2010			2010		
	2009	CR	TR	2009	CR	TR	2009	CR	TR
Hargrand	13.2 ± 0.4	13.7 ± 0.2 a	14.3 ± 0.3 a	2.46 ± 0.15	1.56 ± 0.16 a	1.70 ± 0.10 a	5.4 ± 0.5	8.9 ± 0.7 a	8.3 ± 0.3 a
Harlayne	11.5 ± 1.1	13.1 ± 1.3 a	14.7 ± 0.3 a	1.65 ± 0.05	1.28 ± 0.01 a	1.14 ± 0.04 b	7.0 ± 0.7	10.5 ± 1.3 b	13.0 ± 0.2 a
Harogem	12.9 ± 0.7	11.6 ± 0.1 b	14.5 ± 0.4 a	1.56 ± 0.02	1.01 ± 0.16 a	1.01 ± 0.07 a	8.3 ± 0.5	11.7 ± 2.1 a	14.5 ± 1.0 a
Tomcot <sup>b</sup>	10.5 ± 0.5	–	11.2 ± 0.6	1.81 ± 0.05	–	1.25 ± 0.08	5.8 ± 0.3	–	9.0 ± 0.4
Vivagold	10.6 ± 0.9	12.5 ± 0.7 b	14.1 ± 0.1 a	1.61 ± 0.08	3.45 ± 0.12 a	0.91 ± 0.10 b	6.6 ± 0.8	3.6 ± 0.1 b	15.7 ± 1.8 a

variety	pH			moisture content (%)		
	2010			2010		
	2009	CR	TR	2009	CR	TR
Hargrand	3.08 ± 0.04	3.47 ± 0.04 b	3.68 ± 0.06 a	84.8 ± 0.2	85.6 ± 0.3 a	80.9 ± 0.4 b
Harlayne	3.46 ± 0.03	3.57 ± 0.04 b	3.67 ± 0.04 a	87.0 ± 0.1	86.5 ± 0.9 a	83.9 ± 0.2 b
Harogem	3.18 ± 0.01	3.54 ± 0.04 b	3.69 ± 0.04 a	85.6 ± 0.1	89.0 ± 0.8 a	84.7 ± 0.4 b
Tomcot	3.40 ± 0.02	–	3.48 ± 0.03	87.9 ± 0.3	–	87.8 ± 0.5
Vivagold	3.35 ± 0.03	3.53 ± 0.03 b	3.77 ± 0.01 a	88.2 ± 0.0	84.7 ± 0.1 b	86.3 ± 0.2 a

<sup>a</sup>Within a variety, means not followed by the same letter indicate a significant difference between 2010 commercial ripe and tree ripe fruit for a chemical parameter (Tukey test,  $\alpha = 0.05$ ). <sup>b</sup>'Tomcot' was evaluated only at TR in 2010.

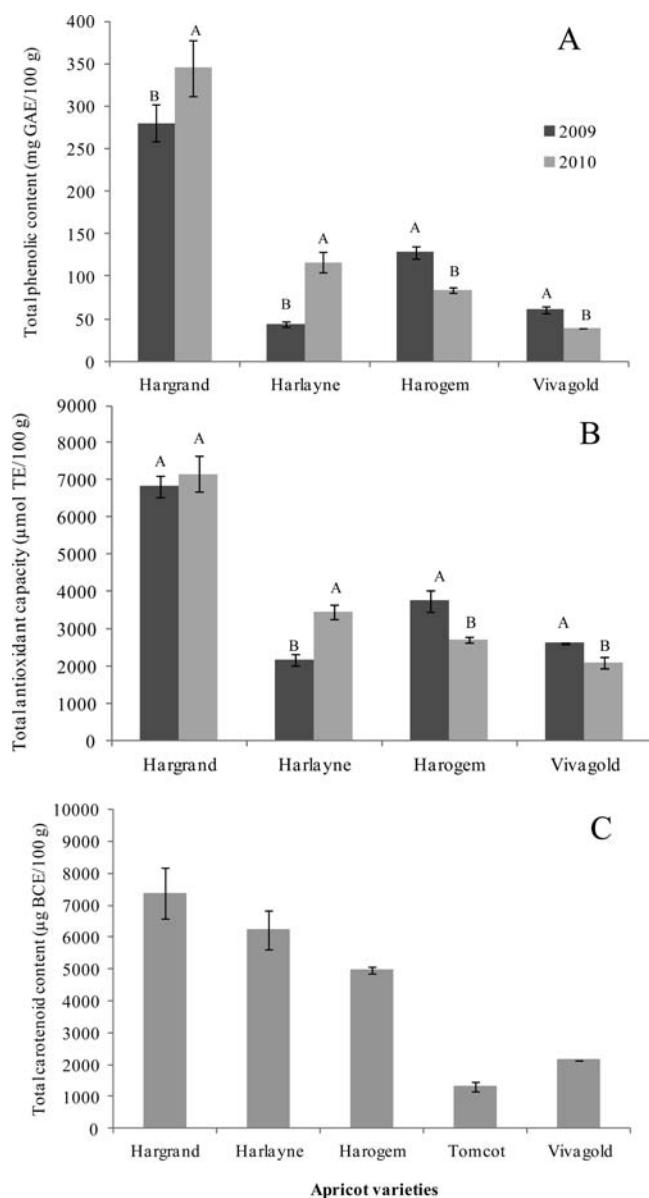
resistance to perennial canker, brown rot and bacterial spot. 'Tomcot', although not considered a reliable commercial variety in this region, was included to compare obtained information with available published data from different regions of cultivation. There was some variation in the harvest dates of varieties in the two years, in response to different climatic conditions in the study years; all varieties were harvested between July 27–August 4 in 2009 and July 16–August 4 in 2010. Given harvest and postharvest conditions and quality parameters, fruit from 2009 was compared to tree-ripened fruit from 2010 for an evaluation of the effect of changes due to seasonal variations. While the influence of maturity at harvest was evaluated for four varieties, the effect of postharvest storage was assessed solely for 'Hargrand', the only variety that retained satisfactory quality after the previously described storage conditions.

Due to the ability of apricots to ripen either on or off the tree, a comparison of commercial ripe (CR) to tree ripe (TR) samples indicated changes occurring when fruit was left to ripen on the tree, while contrasting CR with storage (ST) samples showed changes when fruit was harvested early and stored under cold conditions for extended periods. Comparing ST to TR allowed for a study of the effects of early harvest and subsequent long-term cold storage (as is largely done in commercial fruit production) versus late harvest (for local markets or consumption within days) on fruit properties and constituents. The description of CR in particular differs between regions of production or even orchards, depending on the required shelf life of fruit, which in turn may be influenced by the length of time to consumption or distance over which the produce must be transported to its final market. As such, while orchards in our study required full color development for CR harvest, the practice in other producing areas with a greater output or a wider distribution may require that fruit be harvested while still green.

**Physical Characterization.** Varietal evaluation provided information on the attributes of the selected varieties as they performed in this region (Figure 1). Measured in 2010, the range for fruit weight was 24.4–49.6 g, firmness 6.7–17.7 N, cross-sectional diameter 35.1–47.8 mm and edible portion

91.5–94.4%. 'Tomcot', less cold-hardy than other varieties evaluated, produced small fruit which weighed much less than has been recorded for samples cultivated in Naoussa, Greece (24.4 g compared to 70.9 g).<sup>15</sup> Fruit weight correlated well with size ( $R = 0.86$ ) with the three Harrow varieties having weight and sizes of >48 g and >43 mm, respectively. These varieties were also visually attractive, with 'Harogem' possessing a striking red shade, evident even in its flowers, and 'Harlayne' having a large size and attractive, uniform orange color, properties which have made it a top seller for a major Northeast fruit producer. Color parameters  $a$  and  $b$  were consistently in the positive range indicating red and yellow colors. Given the phenotypic similarity between varieties assessed, peel and flesh color between varieties was not significantly different. Peel color was typically orange, ranging from more yellow ('Tomcot' and 'Vivagold') to more red ('Harogem') shades, reflected in high  $b$  readings for the former group and high  $a$  readings for the latter (Table 1). Differences in color over the two study years were less pronounced in the peel compared to the flesh.

The varieties studied experienced a mean of 60% decrease in firmness from CR to TR (Table 2), with a 73% decrease in 'Hargrand' from CR to ST. The mean TR firmness of 11.7 N (2.6 lb) was within the range of 2–3 lb reported by Crisosto and Kader<sup>27</sup> for 'ready-to-eat' fruit. Given that by our definition of CR, fruit was in the ripening stage and growth had ceased, significant differences in these parameters was not expected between the two harvests.<sup>28,29</sup> However, an increase in fruit weight and size from CR to TR was observed in 'Vivagold' and, in both 'Vivagold' and 'Harogem', edible portion increased with ripening. Fruit was also assessed for possible changes in color of peel and flesh with ripening on- or off-tree; observations or relationships unearthed here could have contributed to the search for nondestructive methods of assessment of apricot maturity. While some significant changes were observed for the various color parameters of some varieties with ripening (Table 1), there were no significant differences in mean peel or flesh color from CR to TR. This stood to reason since one of the criteria for pickers in harvesting CR fruit (in our study orchards) was full color development, and thus striking increases in  $a$  or  $b$ , as occur in the transition from ground



**Figure 2.** (A) Total phenolic content, (B) total antioxidant capacity and (C) total carotenoid content of Northeast apricot varieties evaluated in 2009 and 2010 (GAE: Gallic acid equivalents, TE: Trolox equivalents, BCE:  $\beta$ -carotene equivalents). Bars with different letters indicate a significant difference between the two years (Tukey test,  $\alpha = 0.05$ ).

color, were not present in this case.<sup>28</sup> A greater diversity in colors of varieties and increase in sample points through fruit development would be necessary to observe and/or establish reliable trends.

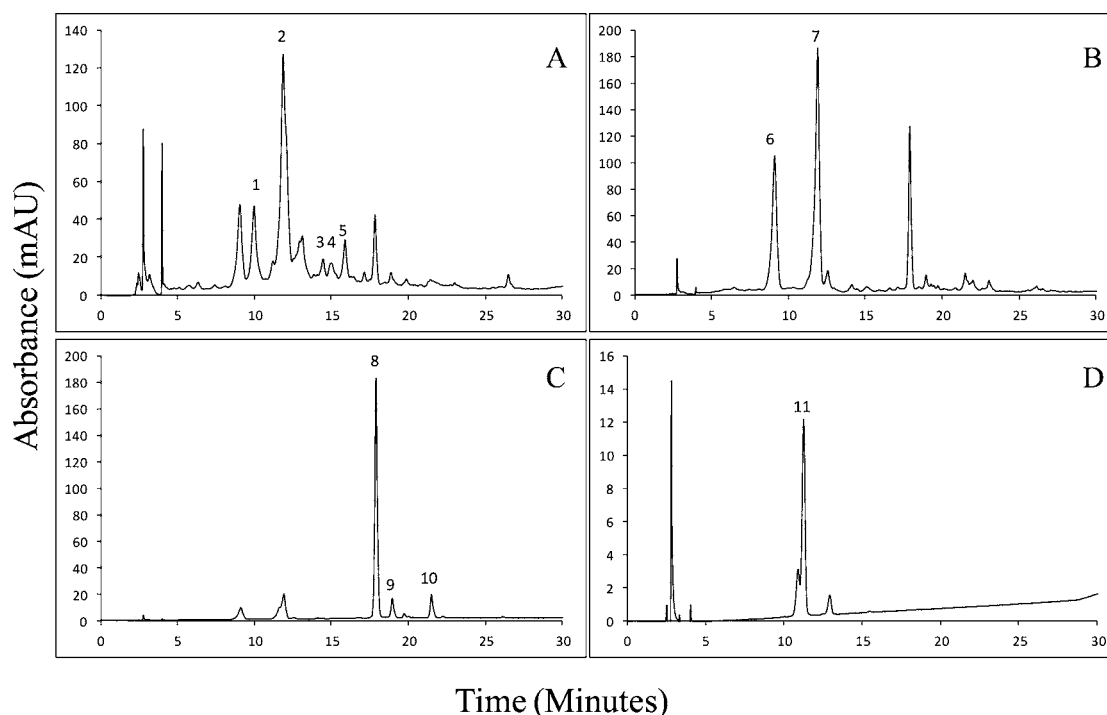
**Chemical Characterization.** Results of chemical analyses were comparable to those from Drogoudi et al.<sup>15</sup> and Aubert and Chanforan<sup>30</sup> for apricot soluble solids content, titratable acidity, sugar-to-acid ratio, moisture content and pH (Table 3). The former study found sucrose to be the predominant sugar in apricots while the latter reported citric and malic as the major organic acids. 'Harlayne' and 'Harogem' ranked high in soluble solids content and sugar-to-acid ratio in both years. In 2010, considering TR samples, varieties generally had higher soluble solids content, sugar-to-acid ratio and pH, and lower moisture content and titratable acidity compared to 2009. This was

attributed in part to differences in climatic conditions between the two years. Average rainfall over the growing season was 2.9 in. in 2009 and 1.8 in. in 2010, with rainfall being copious throughout the 2009 growing season but negligible post-June in 2010.<sup>31</sup> This contributed to a greater concentration of solids in fruit in 2010.<sup>32</sup> As with other stone fruits, rainfall amount and patterns, particularly the water deficit late in the season (during which cell expansion occurs—referred to as stage III of fruit growth) was also implicated in visually smaller fruit in 2010 compared to those in 2009.<sup>33</sup>

Physiological changes as the fruit ripens result in, among other things, changes in sugar (due to sucrose accumulation) and acid concentrations.<sup>34</sup> Overall taste/flavor development and thus consumer acceptance (sensory perception) increases with ripening. This may be gauged instrumentally using the sugar-to-acid ratio, although actual acceptability tests remain the best means of assessment. Mean TR soluble solids content (14.4%) was in line with the value suggested by Crisosto and Kader<sup>27</sup> to be important for consumer acceptance (>10%). From CR to TR (Table 3), there were significant ( $p < 0.01$ ) increases in mean values for soluble solids content (from 12.7 to 14.4%), sugar-to-acid ratio (from 8.7 to 12.9) and pH (from 3.53 to 3.70) and decreases in moisture content (from 86.5 to 84.0%) and titratable acidity (from 1.83 to 1.19 g). These trends were similar to those reported by other studies<sup>29,34,35</sup> although substantial differences were observed in varietal responses with ripening for the various parameters, with an increasing pH being the only consistent significant change. From CR to ST in 'Hargrand', increases in soluble solids (from 13.7 to 14.8%), sugar-to-acid ratio (from 8.9 to 10.6) and pH (from 3.47 to 3.83) and decreases in titratable acidity (from 1.56 to 1.42 g) and moisture content (from 85.6 to 84.3) were observed, with changes in pH and moisture content being significant ( $p \leq 0.01$ ).

**Phenolic Content.** Total phenolic content (TP) of apricots ranged from 44.0 to 280.2 mg in 2009 and 38.6 to 345.1 mg in 2010. These values were within the range of 30.3–559.6 mg by Drogoudi et al.<sup>15</sup> for 29 apricot cultivars of Greek and American origin, using similar methods of analyses. 'Hargrand' consistently stood out in both years, having more than twice the TP of the next closest variety (Figure 2), comparing favorably against values reported for more popular local fruits, including peaches (133 mg) and grapes (170 mg).<sup>36</sup> 'Harlayne' and 'Vivagold' had lowest TP in 2009 and 2010, respectively. Varieties exhibited different responses to conditions in the study years with 'Hargrand' and 'Harlayne' increasing in TP, 'Vivagold' and 'Harogem' decreasing and 'Tomcot' showing no change. Flavan-3-ols were the most diverse and predominant compounds (Figure 3). Ranges for phenolic compounds in 2009 and 2010 respectively, reported as mg/100 g, were as follows: Flavan-3-ols: catechin (3.1–18.5 and 0.2–26.4), epicatechin (1.4–5.8 and 2.0–5.8), epigallocatechin (1.3–9.6 and 3.4–22.7), unknown 1 (0.1–3.7 and 1.1–7.1) and unknown 2 (1.7–7.3 and 2.7–7.1); hydroxycinnamic acids: chlorogenic acid (3.4–15.0 and 2.3–18.4) and neochlorogenic acid (5.6–18.6 and 4.6–12.9); flavonol glycosides: rutin (6.7–14.5 and 4.4–10.8), quercetin-3-glucoside (0.9–1.0 and 0.8–1.3), quercetin derivative (1.0–1.5 and 0.9–1.3); anthocyanins: cyanidin-3-glucoside (0.8–1.2 and 0.9–2.4).

Similar to spectrophotometer-determined TP, changes in HPLC-determined phenolic content (HPLC-TP) in the two study years differed with variety, with increases in 'Hargrand' and 'Harlayne' and decreases in 'Harogem' and 'Vivagold'



**Figure 3.** HPLC chromatograms of an apricot extract showing phenolic compounds at (A) 280 nm, (B) 320 nm, (C) 370 nm and (D) 520 nm. Compounds identified are epigallocatechin (1), catechin (2), unknown 1 (3), epicatechin (4), unknown 2 (5), neochlorogenic acid (6), chlorogenic acid (7), rutin (8), quercetin-3-glucoside (9), quercetin derivative (10) and cyanidin-3-glucoside (11).

(Table 4). A strong correlation ( $R = 0.96$ ) was found between HPLC-TP and spectrophotometer-determined TP, implying that both methods were equivalent gauges of relative varietal phenolic content. Correlations were also found between HPLC-TP and catechin ( $R = 0.95$ ), chlorogenic acid ( $R = 0.88$ ) and epigallocatechin ( $R = 0.81$ ). Levels of these compounds, particularly catechin, may be considered indicative of varietal phenolic content. The varieties exhibited similar phenolic profiles, although anthocyanins were not detected in 'Hargrand' and 'Vivagold', or in 2010 'Tomcot'. 'Harogem', a variety with prominent red peel color, had consistently relatively higher cyanidin-3-glucoside content (approximately twice the concentration of the next highest variety). No significant correlations were found between total phenolic content or individual phenolic compounds and any physical or chemical component; this was thought to be due to the phenotypic similarity of varieties evaluated. However, Ruiz et al.,<sup>3</sup> who evaluated thirty-seven apricots varieties of varying flesh color also reported no correlations between phenolic content and this attribute.

Dragovic-Uzelac et al.<sup>4</sup> reported declines in phenolic content with maturity in three Croatian-grown apricot varieties while Hegedus et al.<sup>16</sup> found significant increases with ripening in two Hungarian varieties. In both studies, results were subject to varietal influence as well as the developmental stages at which fruit samples were harvested and/or evaluated. In our study, TR fruit TP of three varieties was significantly lower than CR fruit TP ( $p < 0.01$  in 'Harlayne' and 'Vivagold',  $p < 0.05$  in 'Harogem') (Figure 5). Suggested reasons for decreases in phenolic content with ripening include a change in their role in the plant, and a necessity to ensure the reduction of astringency for better taste and palatability.<sup>37</sup> The decline could also be attributed to an observed increase in polyphenoloxidase (PPO) activity with fruit maturity.<sup>38</sup> Comparing the three stages in

'Hargrand', no significant differences were seen under the conditions studied.

Changes in individual phenolic compounds and their concentration with ripening were variety-dependent (Table 4). Flavan-3-ols increased in 'Hargrand' and decreased in 'Harlayne' and 'Vivagold', with no significant trend in 'Harogem'; hydroxycinnamic acids decreased in 'Harlayne', 'Harogem' and 'Vivagold' but showed the opposite trend in 'Hargrand'. Flavonol glycosides decreased in 'Harogem' and 'Vivagold' but remained stable in 'Hargrand' and 'Harlayne'. Cyanidin-3-glucoside disappeared in 'Hargrand' and 'Vivagold' (the latter variety also losing epigallocatechin) while it increased in 'Harlayne' and 'Harogem'. HPLC-TP remained highly correlated with spectrophotometer-determined TP ( $R = 0.96$ ) and with catechin, epigallocatechin, chlorogenic acid and neochlorogenic acid ( $R > 0.90$  in all cases). TR 'Hargrand' had higher concentrations of individual compounds compared to CR and ST samples. HPLC analysis therefore confirmed the decline in phenolic content with ripening for all varieties except 'Hargrand'. This deviation could be explained in part by the observation by Barrett<sup>38</sup> that the increase in PPO activity with fruit age was not linear and could be influenced by the specific point in fruit development at which sampling occurred. Additionally, Holderbaum et al.<sup>39</sup> reported that the susceptibility to PPO degradation in apples was genotype-specific and also influenced by a range of factors including the quantity, quality and relative proportions of phenolic compounds.

**Antioxidant Capacity.** In 2009, hydrophilic and lipophilic antioxidant capacities were measured separately in the method described by Prior et al.<sup>40</sup> The highest contribution was found to be from the hydrophilic fraction, correlating highly with total (hydrophilic + lipophilic) antioxidant capacity ( $R = 0.91$ ), with lipophilic compounds contributing only 2% (data not shown). These results were similar to those reported by Wu et al.,<sup>41</sup> who

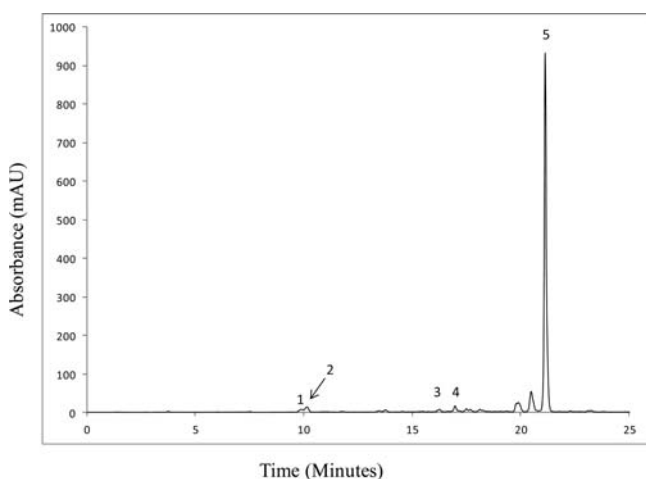
**Table 4. Phenolic Compounds (mg/100 g) in Northeast Apricot Varieties Evaluated in 2009 and at Commercial Ripe (CR), Tree Ripe (TR) and Storage (ST) Stages in 2010 (n = 3)**

compounds <sup>a</sup>	Hargrand				Harlayne		
	2009	2010			2009	2010	
		CR	TR	ST		CR	TR
catechin	18.5 ± 0.4	21.6 ± 0.3 b	26.4 ± 1.2 a	14.4 ± 0.9 c	3.4 ± 0.3	8.7 ± 0.2 a	0.2 ± 0.0 b
chlorogenic acid	15.0 ± 0.3	14.8 ± 0.6 b	18.4 ± 0.1 a	17.0 ± 2.6 a	8.7 ± 0.3	3.4 ± 0.1 a	2.3 ± 0.2 b
cyanidin-3-glucoside	ND <sup>e</sup>	0.8 ± 0.0	ND	ND	0.8 ± 0.0	0.8 ± 0.0 a	0.9 ± 0.0 b
epicatechin	3.6 ± 0.2	2.8 ± 0.2 b	4.1 ± 0.3 a	2.7 ± 0.2 b	1.4 ± 0.1	10.8 ± 0.1 a	5.8 ± 0.4 b
epigallocatechin	9.6 ± 1.0	18.4 ± 0.8 b	22.7 ± 1.1 a	12.5 ± 0.3 c	1.4 ± 0.2	6.6 ± 0.2 a	3.4 ± 0.5 b
neochlorogenic acid	7.0 ± 0.7	10.7 ± 0.6 b	12.9 ± 0.8 a	9.7 ± 0.7 b	5.6 ± 0.2	10.6 ± 0.2 a	6.6 ± 0.7 b
quercetin-3-glucoside	1.1 ± 0.0	1.1 ± 0.1 a	1.3 ± 0.0 a	1.2 ± 0.1 a	0.9 ± 0.0	0.9 ± 0.1 a	0.9 ± 0.1 a
quercetin derivative	1.3 ± 0.0	1.2 ± 0.0 a	1.3 ± 0.0 a	1.2 ± 0.1 a	1.0 ± 0.0	0.9 ± 0.1 a	0.9 ± 0.0 a
rutin	7.8 ± 0.2	9.9 ± 1.1 a	10.8 ± 1.8 a	12.0 ± 1.2 a	6.7 ± 0.4	4.9 ± 0.1 a	4.4 ± 0.4 a
unknown 1 <sup>c,d</sup>	2.0 ± 0.3	8.7 ± 0.7 a	7.1 ± 0.6 a	4.0 ± 0.2 b	0.1 ± 0.0	13.3 ± 0.3 a	6.0 ± 0.9 b
unknown 2 <sup>c,d</sup>	7.3 ± 0.7	6.6 ± 0.5 a	6.6 ± 0.6 a	5.8 ± 0.6 a	1.7 ± 0.1	9.7 ± 0.6 a	5.5 ± 0.6 b
total	73.1 ± 3.8	96.6 ± 4.9 b	111.6 ± 6.5 a	80.5 ± 6.9 c	31.7 ± 1.7	70.6 ± 2.0 a	37.0 ± 3.8 b

compounds	Harogem			Vivagold			Tomcot <sup>b</sup>	
	2009	2010		2009	2010		2009	TR
		CR	TR		CR	TR		
catechin	8.7 ± 0.6	10.3 ± 0.8 a	2.7 ± 0.2 b	3.1 ± 0.0	6.6 ± 1.0 a	2.1 ± 0.0 b	4.6 ± 0.1	6.5 ± 0.6
chlorogenic acid	3.8 ± 0.2	4.0 ± 0.4 a	2.3 ± 0.1 b	3.4 ± 0.3	9.2 ± 0.3 a	3.1 ± 0.0 b	6.3 ± 0.2	5.2 ± 0.8
cyanidin-3-glucoside	1.2 ± 0.0	1.5 ± 0.1 a	2.4 ± 0.3 b	ND	0.9 ± 0.0	ND	0.8 ± 0.1	ND
epicatechin	5.8 ± 0.2	2.6 ± 0.2 b	4.3 ± 0.2 a	1.9 ± 0.0	2.8 ± 0.1 a	2.0 ± 0.1 b	1.4 ± 0.1	2.2 ± 0.1
epigallocatechin	3.6 ± 0.3	6.5 ± 0.6 a	4.7 ± 0.3 b	1.3 ± 0.0	1.4 ± 0.0	ND	1.8 ± 0.1	5.2 ± 0.6
neochlorogenic acid	10.2 ± 0.1	8.1 ± 0.8 a	5.8 ± 0.1 b	8.3 ± 0.8	11.8 ± 0.5 a	4.6 ± 0.1 b	18.6 ± 0.7	12.8 ± 0.9
quercetin-3-glucoside	1.0 ± 0.0	0.9 ± 0.1 a	1.2 ± 0.1 a	0.9 ± 0.0	1.4 ± 0.1 a	0.9 ± 0.0 b	1.0 ± 0.0	0.8 ± 0.0
quercetin derivative	1.3 ± 0.0	1.5 ± 0.0 a	1.0 ± 0.1 b	1.4 ± 0.1	2.2 ± 0.1 a	1.1 ± 0.0 b	1.5 ± 0.1	0.9 ± 0.0
rutin	7.1 ± 0.5	10.6 ± 0.4 a	6.3 ± 0.4 b	9.7 ± 0.9	18.5 ± 0.9 a	4.9 ± 0.1 b	14.5 ± 1.0	4.7 ± 0.1
unknown 1	3.7 ± 0.1	2.6 ± 0.2 b	3.2 ± 0.1 a	1.0 ± 0.2	1.9 ± 0.5 a	1.1 ± 0.1 b	0.6 ± 0.1	2.8 ± 0.4
unknown 2	3.3 ± 0.3	2.4 ± 0.1 b	3.9 ± 0.3 a	2.2 ± 0.1	2.6 ± 0.3 a	2.7 ± 0.1 a	2.9 ± 0.2	7.1 ± 0.5
total	49.6 ± 2.4	51.0 ± 3.7 a	37.8 ± 3.2 b	33.1 ± 2.4	59.3 ± 3.8 a	22.5 ± 0.5 b	54.0 ± 2.7	48.1 ± 4.0

<sup>a</sup>Within a variety, means not followed by the same letter indicate a significant difference between 2010 commercial ripe and tree ripe fruit (and storage for Hargrand) for a phenolic compound (Tukey test,  $\alpha = 0.05$ ). <sup>b</sup>Tomcot<sup>b</sup> was evaluated only at TR in 2010. <sup>c,d</sup>Unknowns 1 and 2 are flavan-3-ols. <sup>e</sup>ND: Not detected.



**Figure 4.** HPLC chromatogram of an apricot extract showing carotenoid compounds at 450 nm. Identified compounds are zeaxanthin (1), lutein (2), unknown (3),  $\beta$ -cryptoxanthin (4) and  $\beta$ -carotene (5).

found the ORAC lipophilic fraction to be 2.4% of total apricot antioxidant capacity. Thereafter, 2009 total antioxidant capacity (AOX) was re-evaluated as described by Huang et al.,<sup>23</sup> and the

same methodology used in 2010 (Figure 2). Strong correlations were found between AOX and both spectrophotometric TP ( $R = 0.96$ ) and HPLC-TP ( $R = 0.92$ ), agreeing with previous studies.<sup>15,40</sup> Accordingly, the variety with greatest phenolic content in both years, 'Hargrand', had the greatest AOX (6282.2 and 7165.1  $\mu\text{mol}$  in 2009 and 2010 respectively) while 'Harlayne' and 'Vivagold' were lowest in the two years (2182.2 and 2096.9  $\mu\text{mol}$ , respectively). There was no set trend in varietal AOX response to the rainfall variations in the two years and other factors, including variety and maturity at harvest, were suggested to be more influential.

As with phenolic content, AOX correlated best with catechin ( $R = 0.91$ ), chlorogenic acid ( $R = 0.83$ ) and epigallocatechin ( $R = 0.80$ ); catechin and chlorogenic acid had previously been found to relate significantly with apricot AOX.<sup>42</sup> It is difficult to compare these AOX values with those from other studies, mainly due to the various methods by which antioxidant capacity is measured. AOX values surpassed those given by Wu et al.<sup>41</sup> (1341  $\mu\text{mol}$ ) and Kevers et al.<sup>43</sup> (1027  $\mu\text{mol}$ ); both studies used unidentified apricot varieties. Values for 'Hargrand' in both years, as well as 'Harogem' and 'Tomcot' in 2009 and 'Harlayne' in 2010, also exceeded ORAC values reported for apples (3000  $\mu\text{mol}$ ) and grapes (2000  $\mu\text{mol}$ ),<sup>36</sup> positioning 'Hargrand' in particular as a good source of antioxidants.

**Table 5. Carotenoid Compounds ( $\mu\text{g}/100\text{ g}$ ) and Vitamin A Retinol Activity Equivalents ( $\mu\text{g}/100\text{ g}$ ) in Northeast Apricot Varieties Evaluated at Commercial Ripe (CR), Tree Ripe (TR) and Storage (ST) Stages in 2010 ( $n = 3$ )**

compounds <sup>a</sup>	Hargrand			Harlayne	
	CR	TR	ST	CR	TR
beta-carotene	1041.7 $\pm$ 77.8 c	7174.5 $\pm$ 763.4 a	5930.9 $\pm$ 565.5 b	1665.8 $\pm$ 154.3 b	5600.3 $\pm$ 116.8 a
beta-cryptoxanthin	12.4 $\pm$ 2.9 c	31.6 $\pm$ 3.9 a	24.5 $\pm$ 3.5 b	12.1 $\pm$ 2.8 b	41.1 $\pm$ 8.1 a
lutein	8.4 $\pm$ 0.8 a	10.5 $\pm$ 1.1 a	11.9 $\pm$ 1.4 a	7.3 $\pm$ 0.5 b	12.0 $\pm$ 0.1 a
zeaxanthin	107.6 $\pm$ 2.8 a	238.7 $\pm$ 10.5 b	ND <sup>d</sup>	ND	104.0 $\pm$ 8.4
unknown	9.6 $\pm$ 1.8 b	26.3 $\pm$ 2.7 a	35.6 $\pm$ 10.4 a	18.8 $\pm$ 0.8 b	28.9 $\pm$ 5.0 a
vitamin A, RAE <sup>c</sup>	87.3 $\pm$ 6.6 b	599.2 $\pm$ 55.4 a	495.3 $\pm$ 47.3 a	139.3 $\pm$ 13.0 b	468.4 $\pm$ 9.9 a

compounds	Harogem		Vivagold		Tomcot <sup>b</sup>
	CR	TR	CR	TR	TR
beta-carotene	1234.9 $\pm$ 35 b	4361.3 $\pm$ 148.4 a	687.0 $\pm$ 64.4 b	1971.6 $\pm$ 50.5 a	1147.4 $\pm$ 74.4
beta-cryptoxanthin	9.3 $\pm$ 0.3 b	31.2 $\pm$ 3.4 a	8.7 $\pm$ 0.9 b	13.9 $\pm$ 0.0 a	8.0 $\pm$ 0.5
lutein	13.3 $\pm$ 1.6 a	10.0 $\pm$ 0.3 b	5.6 $\pm$ 0.1 b	7.4 $\pm$ 1.0 a	7.9 $\pm$ 0.6
zeaxanthin	68.3 $\pm$ 5.2 b	94.8 $\pm$ 7.0 a	ND	ND	ND
unknown	6.6 $\pm$ 0.1 b	40.7 $\pm$ 8.4 a	63.0 $\pm$ 5.2 a	66.7 $\pm$ 0.8 a	68.2 $\pm$ 9.5
vitamin A, RAE	103.3 $\pm$ 2.9 b	364.8 $\pm$ 29.2 a	57.6 $\pm$ 5.4 b	164.9 $\pm$ 4.2 a	95.95 $\pm$ 6.2

<sup>a</sup>Within a variety, means not followed by the same letter indicate a significant difference between 2010 commercial ripe and tree ripe fruit (and storage for Hargrand) for a carotenoid compound (Tukey test,  $\alpha = 0.05$ ). <sup>b</sup>'Tomcot' was evaluated only at TR in 2010. <sup>c</sup>RAE: Retinol activity equivalents (1  $\mu\text{g}$  RAE = 12  $\mu\text{g}$  beta-carotene or 24  $\mu\text{g}$  beta-cryptoxanthin). <sup>d</sup>ND: Not detected.

Given the significant correlation between TP and AOX, similar results as seen with phenolics were expected (i.e., decline or relative stability of phenolics with ripening). 'Hargrand' and 'Harogem', which had experienced no or little phenolic content decline with ripening, did not change significantly in AOX with ripening. 'Harlayne' and 'Vivagold' AOX decreased with ripening ( $p < 0.01$ ), contrary to findings by Hegedus et al.<sup>16</sup> and Bartolini et al.,<sup>44</sup> who studied two and three apricot varieties, respectively, using the ferric reducing antioxidant plasma (FRAP) assay. While Bartolini et al. also observed a decrease with cold storage ( $4 \pm 1$  °C for 7 and 15 days), there were no significant differences in 'Hargrand' AOX with ripening or storage.

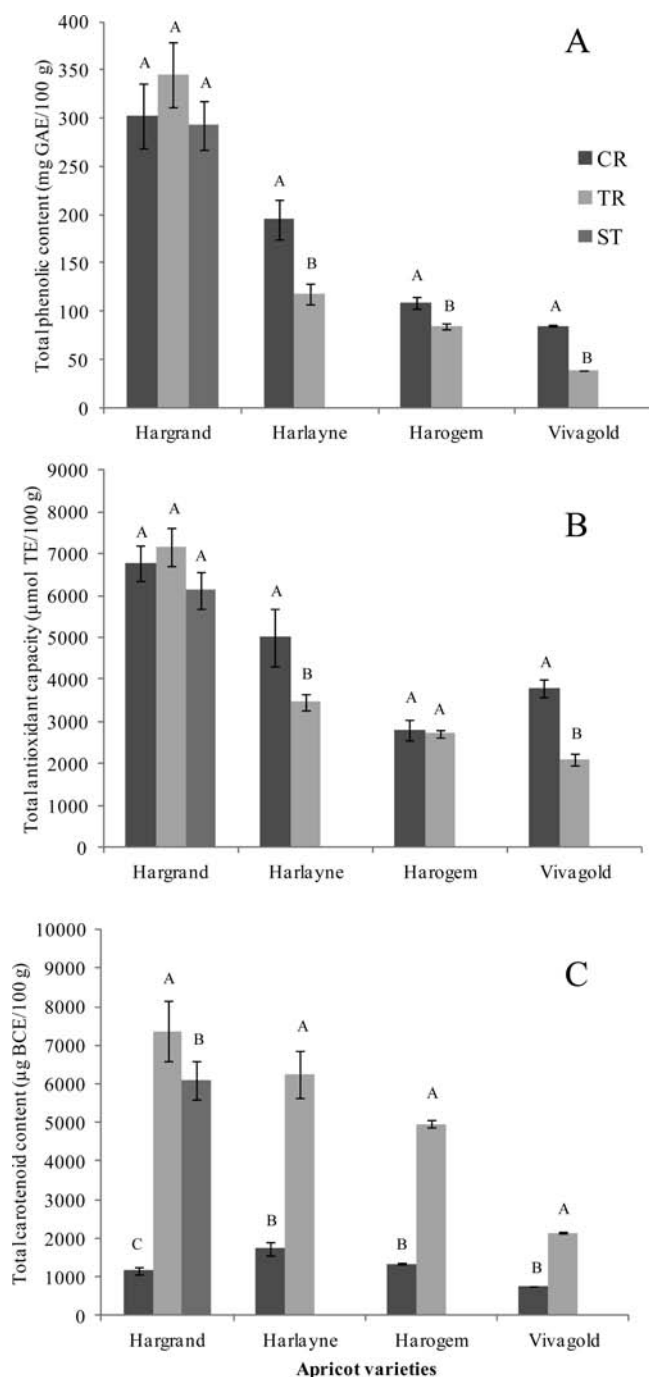
**Carotenoid Content.** An initial assessment of total carotenoid content (TC) was conducted in 2009 (data not shown). Varietal ranking that year was, in decreasing order, 'Hargrand', 'Harogem', 'Vivagold', 'Tomcot' and 'Harlayne'. The methodology employed was discontinued due to poor reproducibility, and a procedure based on methods by Craft et al.<sup>24</sup> was used in 2010 (Figure 2). 'Hargrand' had highest TC (7371.1  $\mu\text{g}$  BCE) and 'Tomcot', a variety not suited for cold climates, the lowest (1312.1  $\mu\text{g}$  BCE). A summation of compounds concentrations resulted in the range 1231.5–7481.6  $\mu\text{g}$ ; within this range fell the value used by the USDA carotenoid database<sup>45</sup> and originally reported by Khachik et al.<sup>46</sup> for apricots of an unidentified variety (6580  $\mu\text{g}$ ). Ruiz et al.<sup>6</sup> provided a much wider range for 25 light-orange and orange fleshed apricot varieties produced in Spain (4920–16500  $\mu\text{g}$ ). The variations in reported values are due to the differences in extraction and quantification methodologies, varieties used and sample maturity, as reported by Dragovic-Uzelac et al.<sup>4</sup> The humid continental climate of the Northeast USA was also implicated in decreased carotenogenesis, given findings by Rodriguez-Amaya et al.<sup>47</sup> of higher carotenoid concentrations in mango and papaya varieties produced in regions in Brazil with elevated temperatures when compared to the same varieties grown in cooler climates. However, using values both from our study and the database compiled by Holden et al.,<sup>45</sup> apricot TC remained higher than those of other

more-frequently consumed fruits. Relationships observed by Ruiz et al.<sup>6</sup> between color parameter *a* of flesh ( $R = 0.93$ ) as well as hue angle of peel ( $R = 0.84$ ) and total carotenoid content were not observed in our study, nor were any strong correlations with any other peel or flesh color parameter, possibly due to varietal phenotypic similarity. Despite the low contribution from lipophilic constituents to total antioxidant content, a correlation of  $R = 0.75$  was found between TC and AOX.

Four carotenoid compounds were identified and quantified (Figure 4) and the concentrations of one unidentified but prominent compound also recorded.  $\beta$ -carotene was the predominant carotenoid compound, accounting for at least 90% of quantified carotenoid content in all varieties and having a strong correlation ( $R = 0.98$ ) with TC. Although reported in some varieties in other studies,<sup>6,7,46</sup> lycopene was not detected in our samples; zeaxanthin content was variety-dependent, being absent in 'Tomcot' and 'Vivagold' (Table 5).

In all varieties, sharp increases in carotenoid content were observed from CR to TR (Figure 5). Similar results have been reported by Dragovic-Uzelac et al.,<sup>4</sup> Katayama et al.<sup>7</sup> and Salunkhe et al.<sup>35</sup> This phenomenon has been attributed to an upregulation of carotenoid gene expression (phytoene synthase) with ripening.<sup>10</sup> The enzyme catalyzes the first committed step of carotenoid synthesis, the conversion of geranylgeranyl pyrophosphate to phytoene; phytoene serves as a precursor of lycopene from which several other carotenoid compounds are synthesized. Of the three categories of bioactive compounds evaluated in this study, carotenoids were the only group to show significant change under cold storage, with 'Hargrand' TC increasing 5-fold from CR to ST. Increase in TC with on-tree ripening ranged from 3-fold in 'Vivagold' to 6-fold in 'Hargrand'. The degree of carotenoid increase with apricot ripening was an important finding as it has significant implications for how production practices (early versus late harvesting) or personal preferences (e.g., eating unripe fruit) affect the amount of vitamin A available to consumers. Additionally, given the time between 'Hargrand' CR and TR (6 days) and CR and ST (four weeks), our results seem to





**Figure 5.** (A) Total phenolic content, (B) total antioxidant capacity and (C) total carotenoid content of Northeast apricot varieties evaluated in 2010 (GAE: Gallic acid equivalents, TE: Trolox equivalents, BCE:  $\beta$ -carotene equivalents). Bars with different letters indicate a significant difference between stages of maturity (Tukey test,  $\alpha = 0.05$ ).

suggest that tree-ripened fruit may be a better source of vitamin A, considering the rapid increase that occurred with on-tree ripening. It would be beneficial in future studies to assess the progression of carotenoid accumulation under cold storage to determine if there is an optimum shelf life for apricots under such conditions in terms of carotenoid content. Consistent increases with ripening were observed in  $\beta$ -carotene and  $\beta$ -cryptoxanthin (Table 5).<sup>7</sup>  $\beta$ -carotene remained the predom-

inant carotenoid and main determinant of fruit carotenoid content; the marked increases in TC were due to the increases in the concentration of this compound. Zeaxanthin was found to be influenced by maturity at harvest (in 'Harlayne' and 'Vivagold') and postharvest storage (in 'Hargrand').

A major appeal of apricots remains their provitamin A content. This was evaluated taking into consideration the recommended dietary allowance (RDA) of 900  $\mu\text{g}$  retinol activity equivalent (RAE) for males 14 years and older, and accepted methods of calculation of dietary provitamin A (1 RAE = 12  $\mu\text{g}$   $\beta$ -carotene or 24  $\mu\text{g}$   $\beta$ -cryptoxanthin).<sup>48,49</sup> A 100 g serving of CR apricots supplied 6–15% RDA. With increases as fruit ripened, TR fruit provided 18–67%, making these varieties good ('Vivagold') or excellent ('Harogem', 'Vivagold', 'Harlayne' and 'Hargrand') sources of vitamin A. An RDA of 55% in stored 'Hargrand' showed that both on-tree and off-tree ripening yield fruit with considerable vitamin A content.

In conclusion, this study provided important information on commercial apricot varieties cultivated in the Northeast USA and proved them noteworthy sources of beneficial phytochemicals. We identified 'Hargrand' apricot as having particularly high phenolic, antioxidant and carotenoid content. Selected flavan-3-ols (catechin and epigallocatechin) and hydroxycinnamic acids (chlorogenic and neochlorogenic acid) proved good indicators of varietal phenolic and antioxidant content, while  $\beta$ -carotene was most indicative of carotenoid content. 'Hargrand' consistently compared favorably against some more popular fruits in phenolic content and antioxidant capacity. All tree-ripe apricot varieties assessed represent good or excellent sources of vitamin A. Seasonal variations influenced some quality indices but had less categorical influences on bioactive compound concentration. Varieties differed in the responses of their phenolic and antioxidant components to ripening, although a trend of decreasing phenolic content was observed in the majority of varieties. In all varieties, a large increase in carotenoid content, and consequently vitamin A, was found in tree-ripened fruit compared to fruit harvested at commercial maturity. The effects of varietal and harvest variations on bioactive compounds illustrated the susceptibility of these compounds to horticultural practices, and highlighted the need for better understanding and, where possible, control of these in order to ensure optimum levels of fruit phytochemicals.

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## REFERENCES

(1) Kader, A. A.; Barrett, D. M. Classification, composition of fruits and postharvest maintenance of quality. In *Processing fruits*, 2nd ed.;

Barrett, D. M., Somogyi, L., Ramaswamy, H., Eds; CRC Press: Boca Raton, FL, 2005; pp 1–21.

(2) *Dietary guidelines for Americans 2010*; United States Department of Agriculture and Department of Health and Human Services: Washington, D.C., 2010; pp 33–53.

(3) Ruiz, D.; Egea, J.; Gil, M.; Tomas-Barberan, F. A. Characterization and quantification of phenolic compounds in new apricot (*Prunus armeniaca* L.) varieties. *J. Agric. Food Chem.* **2005**, *53*, 9544–9552.

(4) Dragovic-Uzelac, V.; Levaj, B.; Mrkic, V.; Bursac, D.; Boras, M. The content of polyphenols and carotenoids in three apricot cultivars depending on stage of maturity and geographical region. *Food Chem.* **2007**, *102*, 966–975.

(5) Radi, M.; Mahrouz, M.; Jaouad, A.; Tacchini, M.; Aubert, S.; Hugues, M.; Amiot, M. J. Phenolic composition, browning susceptibility and carotenoid content of several apricot cultivars at maturity. *HortScience* **1997**, *32*, 1087–1091.

(6) Ruiz, D.; Egea, J.; Tomas-Barberan, F. A.; Gil, M. Carotenoids from new apricot (*Prunus armeniaca* L.) varieties and their relationship with flesh and skin color. *J. Agric. Food Chem.* **2005b**, *53*, 6368–6374.

(7) Katayama, T.; Nakayama, T. O. M.; Lee, T. H.; Chichester, C. O. Carotenoid transformations in ripening apricots and peaches. *J. Food Sci.* **1971**, *36*, 804–806.

(8) Breithaupt, D. E.; Bamedi, A. Carotenoid esters in vegetables and fruits: a screening with emphasis on  $\beta$ -cryptoxanthin esters. *J. Agric. Food Chem.* **2001**, *49*, 2064–2070.

(9) Ames, B. N.; Shigenaga, M. K.; Hagen, T. M. Review: Oxidants, antioxidants, and the degenerative diseases of aging. *Proc. Natl. Acad. Sci. U.S.A.* **1993**, *90*, 7915–7922.

(10) Fraser, P. D.; Bramley, P. M. Review: The biosynthesis and nutritional uses of carotenoids. *Prog. Lipid Res.* **2004**, *43*, 228–265.

(11) Noratto, G.; Porter, W.; Byrne, D.; Cisneros-Zevallos, L. Identifying peach and plum polyphenols with chemopreventive potential against estrogen-independent breast cancer cells. *J. Agric. Food Chem.* **2009**, *57*, 5219–5226.

(12) Landrum, J. T.; Bone, R. A. Minireview: Lutein, zeaxanthin and the macular pigment. *Arch. Biochem. Biophys.* **2001**, *385*, 28–40.

(13) Potter, J. D.; Slattery, M. L.; Bostick, R. M.; Gapstur, S. M. Colon cancer: a review of the epidemiology. *Epidemiol. Rev.* **1993**, *15*, 499–545.

(14) Rao, A. V.; Agarwal, S. Role of antioxidant lycopene in cancer and heart disease. *J. Am. Coll. Nutr.* **2000**, *19*, 563–569.

(15) Drogoudi, P. D.; Vemmos, S.; Pantelidis, G.; Petri, E.; Tzoutzoukou, C.; Karayiannis, I. Physical characters and antioxidant, sugar and mineral nutrient contents in fruit from 29 apricot (*Prunus armeniaca* L.) cultivars and hybrids. *J. Agric. Food Chem.* **2008**, *56*, 10754–10760.

(16) Hegedus, A.; Pfeiffer, P.; Papp, N.; Abranko, L.; Blazovics, A.; Pedryc, A.; Stefanovits-Banyai, E. Accumulation of antioxidants in apricot fruit through ripening: Characterization of a genotype with enhanced functional properties. *Biol. Res.* **2011**, *44*, 339–344.

(17) Perez, A.; Plattner, K.; Baldwin, K. Fruit and tree nuts outlook. United States Department of Agriculture Economic Research Service. Outlook No. (FTS-348); United States Department of Agriculture: Washington, D.C., 2011; pp 12–14

(18) Lamb, R. C.; Stiles, W. C. Apricots for New York State. New York's Food and Life Sciences Bulletin. Cornell University NYSAES: Ithaca, NY, 1983; No. 100, pp 1–4.

(19) Layne, R. E. C.; Bailey, C. H.; Hough, L. F. Apricots. In *Tree and tropical fruits, Fruit breeding*; Vol. 1; Janick, J., Moore, J. N., Eds; Wiley and Sons: New York, 1996; pp 79–112.

(20) Kim, D.-O.; Lee, C. Y. Extraction and isolation of polyphenolics. In *Current protocols in food analytical chemistry*; Wrolstad, R. E., Ed.; John Wiley and Sons: New York, 2002; II.2.1–II.2.12.

(21) Singleton, V. L.; Rossi, J. A. Colorimetry of total phenolics with phosphomolybdic-phosphotungstic acid reagents. *Am. J. Enol. Vitic.* **1965**, *16*, 144–158.

(22) Kim, D.-O.; Padilla-Zakour, O. I. Processing effect on phenolics and antioxidant capacity in anthocyanin-rich fruits: Cherry, plum, and raspberry. *J. Food Sci.* **2004**, *69*, S395–S400.

(23) Huang, D.; Ou, B.; Hampsch-Woodill, M.; Flanagan, J.; Prior, R. High-throughput assay of oxygen radical absorbance capacity assay using fluorescein as the fluorescent probe. *J. Agric. Food Chem.* **2002**, *49*, 4619–4626.

(24) Craft, N. E. Chromatographic techniques for carotenoid separation. In *Handbook of food analytical chemistry, water, pigments, colorants, flavors, texture and bioactive, food components*; Wrolstad, R. E., Acree, T. E., Decker, E. A., Penner, M. H., Reid, D. S., Schwartz, S. J., Shoemaker, C. F., Smith, D., Sporns, F., Eds; John Wiley and Sons: Hoboken, NJ, 2005; pp 91–106.

(25) Kwasniewski, M.; Vanden Heuvel, J.; Pan, B.; Sacks, G. Timing of cluster light environment manipulation during grape development affects C13 norisoprenoid and carotenoid concentrations in Riesling. *J. Agric. Food Chem.* **2010**, *58*, 6841–6849.

(26) Goodwin, T. W. In *Chemistry and biochemistry of plant pigments*, 2nd ed.; Goodwin, T. W., Ed.; Academic Press: New York, 1976; Vol. 1, pp 200–211.

(27) Crisosto, C. H.; Kader, A. A. Apricot: Postharvest quality maintenance guidelines. *Fresh Produce Facts* **1999**, <http://postharvest.ucdavis.edu/produce/producefacts/>.

(28) Femenia, A.; Sanchez, E. S.; Simal, S.; Rossello, C. Developmental and ripening-related effects on the cell wall of apricot (*Prunus armeniaca*) fruit. *J. Sci. Food Agric.* **1998**, *77*, 487–493.

(29) Gomez, E.; Ledbetter, C. A. Development of volatile compounds during fruit maturation: characterization of apricot and plum x apricot hybrids. *J. Sci. Food Agric.* **1997**, *74*, 541–546.

(30) Aubert, C.; Chanforan, C. Postharvest changes in physicochemical properties and volatile constituents of apricot (*Prunus armeniaca* L.). Characterization of 28 cultivars. *J. Agric. Food Chem.* **2007**, *55*, 3074–3082.

(31) Network for environment and weather applications (NEWA). Weather data 2012; <http://newa.cornell.edu/index.php?page=all-weather-data>

(32) Perez-Pastor, A.; Ruiz-Sanchez, M. C.; Martinez, J. A.; Nortes, P. A.; Artes, F.; Domingo, R. Effect of deficit irrigation on apricot fruit quality at harvest and during storage. *J. Sci. Food Agric.* **2007**, *87*, 2409–2415.

(33) Behboudian, M. H.; Mills, T. M. Deficit irrigation in deciduous orchards. In *Horticulture Reviews*; Janick, J., Ed.; John Wiley and Sons: Hoboken, NJ, 1997; Vol. 21, pp 105–131.

(34) Bureau, S.; Chahine, H.; Gouble, B.; Reich, M.; Albagnac, G.; Audergon, J. M. Fruit ripening of contrasted apricot varieties: physical, physiological and biochemical changes. Proceedings of the XIIth Symposium on Apricot. *Acta Horticulturae*; Audergon, J. M., Ed.; 2006; Vol. 701, pp 511–516.

(35) Salunkhe, D. K.; Deshpande, P. B.; Do, J. Y. Effects of maturity and storage on physical and biochemical changes in peach and apricot fruits. *J. Hort. Sci.* **1968**, *43*, 235–242.

(36) USDA database for the oxygen radical absorbance capacity (ORAC) of selected foods, Release 2. United States Department of Agriculture Agricultural Research Service: Washington, D.C., 2010; pp 1–46.

(37) Dalla Valle, A.; Mignani, I.; Spinardi, A.; Galvano, F.; Ciappellano, S. The antioxidant profile of three different peaches cultivars (*Prunus persica*) and their short-term effect on antioxidant status in humans. *Eur. Food Res. Technol.* **2007**, *225*, 167–172.

(38) Barret, R. Characterization of apricot polyphenoloxidase during fruit development. MASC Dissertation; University of Adelaide: Adelaide, Australia, 2002.

(39) Holderbaum, D. F.; Kon, T.; Guerra, M. P. Enzymatic browning, polyphenol oxidase activity, and polyphenols in four apple cultivars: Dynamics during fruit development. *HortScience* **2010**, *45*, 1150–1154.

(40) Prior, R. L.; Hoang, H.; Gu, L.; Wu, X.; Bacchiocca, M.; Howard, L.; Hampsch-Woodill, M.; Huang, D.; Ou, B.; Jacob, R. Assays for hydrophilic and lipophilic antioxidant capacity (ORACFL)

of plasma and other biological and food samples. *J. Agric. Food Chem.* **2003**, *51*, 3273–3279.

(41) Wu, X.; Beecher, G. R.; Holden, J. M.; Haytowitz, D. B.; Gebhardt, S. E.; Prior, R. L. Lipophilic and hydrophilic antioxidant capacities of some common foods in the United States. *J. Agric. Food Chem.* **2004**, *52*, 4026–4037.

(42) Roussos, P. A.; Sefferou, V.; Denaxa, N. K.; Tsantili, E.; Stathis, V. Apricot (*Prunus armeniaca* L.) fruit quality attributes and phytochemicals under different crop load. *Sci. Hort.* **2011**, *129*, 472–478.

(43) Kevers, C.; Falkowski, M.; Tabart, J.; Defraigne, J.-O.; Dommes, J.; Pincemail, J. Evolution of antioxidant capacity during storage of selected fruits and vegetables. *J. Agric. Food Chem.* **2007**, *55*, 8596–8603.

(44) Bartolini, S.; Zanol, S.; Viti, R. Apricot cultivars and cold storage affect the total antioxidant capacity and glutathione content in fruit. Proceedings of the XIIIth IS on Apricot Breeding and Culture. *Acta Horticulturae*; Romojaró, F., Dicenta, F., Martínez-Gómez, P., Eds.; 2006; Vol. 862, pp 359–362.

(45) Holden, J. M.; Eldridge, A. L.; Beecher, G. R.; Buzzard, M.; Bhagwat, S.; Davis, C. S.; Douglas, L. W.; Gebhardt, S.; Haytowitz, D.; Schakel, S. Carotenoid content of U.S. foods: An update of the database. *J. Food Comp. Anal.* **1999**, *12*, 169–196.

(46) Khachik, F.; Beecher, G. R.; Lusby, W. R. Separation, identification and quantification of the major carotenoids in extracts of apricots, peaches, cantaloupe, and pink grapefruit by liquid chromatography. *J. Agric. Food Chem.* **1989**, *37*, 1465–1473.

(47) Rodríguez-Amaya, D. B.; Kimura, M.; Godoy, H. T.; Amaya-Farfan, J. Updated Brazilian database on food carotenoids: Factors affecting carotenoid composition. *J. Food Comp. Anal.* **2008**, *21*, 445–463.

(48) Dietary Supplement Fact Sheet - Vitamin A and Carotenoids. National Institutes of Health, Office of Dietary Supplements: Washington, D.C., 2006.

(49) Dietary Reference Intakes (DRIs): Recommended Dietary Allowances and Adequate Intakes. United States Department of Agriculture Food and Nutrition Center.: Washington, D.C., 2011.