# **Melatonin, Phenolics, and Fruit Quality in Tart Cherries**

## Nana Yaa Asante<sup>1</sup>, Tori Meakem<sup>2</sup>, and Benjamin Gutierrez<sup>2</sup>



<sup>2</sup>United State Department of Agriculture - Agricultural Research Service, Plant Genetic Resources Unit Geneva, NY 14456

#### Introduction

This study aims to measure diversity in melatonin, phenolic compounds, and assess fruit quality across different cultivars of sweet cherries (Prunus avium) and tart cherries (P. cerasus), as well as wild cherry relatives maintained in the USDA Tart Cherry Collection in Geneva, NY. Sweet and tart cherries are known to provide a dietary antioxidants and health-promoting compounds. Melatonin, an endogenous hormone, plays a role in broad-spectrum antioxidative defense and the sleep-wake cycle in mammals and was only discovered to be produced by plants relatively recent in 1995 (Hattori et al., 1995). Phenolic compounds provide defense against biotic and abiotic stressors and contain antioxidative, anti-inflammatory, and anticancer properties. Fruit quality traits such as acidity and sweetness play a big role in consumer preference for cultivars. The evaluation of melatonin, phenolics, malic acid, and soluble sugars in diverse tart cherry cultivars is yet to be done, and this study aims to provide that information for researchers and cherry producers.



#### **Total Phenolics Composition**



Phenolics: Anthocyanins and phenolic acids are more prevalent in cherries than flavonols (Fig. 3). P. cerasus, a hybrid of P. avium and P. fruticosa, contains the highest average of total anthocyanins at 836.6 µg/g FW out of the three species (Table 1). *P. avium* contains the most total phenolic acids at an average of 994  $\mu$ g/g. P. fruticosa at the highest average of total flavonols out of the three species at 209.6  $\mu$ g/g FW (Fig. 3).

HOBART AND

WILLIAM SMITH

COLLEGES

	Anthocyanins	Phenolic Acids	Flavonols
P. avium	460.84	994.15	59.17
P. cerasus	836.59	845.32	141.11
P. fruticosa	575.88	488.1	209.56

**Table 1:** Total Phenolics Composition of 3 cherry species.



Species

Figure 3: Total phenolics composition of *P. avium, P.* cerasus, and P. fruticosa.



Quality and Taste Test: There is no significant relationship between malic acid and soluble sugars across cultivars in the 3 cherry species (Fig. 4). The sugar-acid ratio has no effect on consumer preference (Fig. 5). Tart cherry accession 'Itt 18 (12)' had the second highest sugar-acid ratio, but the highest rating by consumers (Fig.5c). Accession 'Tschernokorka' has the lowest sugar-acid ratio and lowest consumer rating (Fig 5a). 'Montmorency', the most consumed cherry in the US, had the highest sugar-acid ratio, but not a high consumer rating (Fig. 5b).



#### **Materials and Methods**

- Fruit samples were obtained from the USDA-ARS Tart Cherry Collection at peak maturity. A total of 103 accessions were studied.
- Melatonin identification: samples extracted in 100% methanol, shaken for 30 • minutes, passed through a 0.22 um filter, separated using a C18 column, and detected using High-Performance Liquid Chromatography (HPLC) with a fluorescence detector (Xia et al., 2020). Samples were run through a qTOF Mass Spectrometer to verify the presence of melatonin.
- <u>Phenolics</u>: samples extracted in methanol, separated with a C18 column, and detected using HPLC with a diode array detector.
- Malic acid and Brix: Samples were juiced, measured with an auto-titrator with 0.1 N NaOH and endpoint pH of 8.2, and converted to malic acid using neutralization equivalent value of 67.04 g malic acid per mole of NaOH. Brix determined with a digital refractometer.
- Taste Test: 7 tart cherry accessions sampled by UDSA-ARS members and ranked from 1-10, where 10 is the best.

### Results



the melatonin fragments of the melatonin

standard to mature and immature fruit

samples.

Melatonin identification: The methods for melatonin analysis were insufficient in identifying and quantifying melatonin (Fig. 1). A peak was present at 5.7 min in the immature fruit sample (Fig. 2), but the mass spectrum did not correlate to melatonin fragments (Fig. 1).



**Diagram 1:** Melatonin chemical structure.

Figure 4: The relationship between malic acid and soluble sugars of cherry cultivars across the 3 species. ( $R^2$ = 0.01, p-value = 0.24)





Figure 5: The relationship between Brix to malic acid ratio of cherry cultivars across the 3 species. ( $R^2 = 0.6$ , p-value = 0.058)



#### Discussion

Further trials in the procedure of melatonin analysis should be conducted, starting with a different extraction method. Future studies can include comparing the abundance of melatonin to the abundance of phenolic compounds to see the relationship between these antioxidative substances.

Accessions that are highly preferred by consumers have a high sugar to acidity ratio whereas the least preferred have a low sugar to acidity ratio. 'Montmorency', the most widely produced tart cherry in America, was among the bottom-ranked in the taste test. A greater sample size should be used in future taste tests as well as choosing a wider cherry variation of sugar-acid ratios.



#### References



Figure 2: Chromatogram of melatonin identification. A melatonin standard was compared to mature and immature tart cherry fruit.

- Hattori, A., H. Migitaka, M. ligo, M. Itoh, K. Yamamoto, R. Ohtani-Kaneko, M. Hara, T. Suzuki, and R. J. Reiter. "Identification of Melatonin in Plants and Its Effects on Plasma Melatonin Levels and Binding to Melatonin Receptors in Vertebrates." Biochemistry and Molecular Biology International 35, no. 3 (March 1995): 627–34.
- Quero-García, J., Amy lezzoni, J. Puławska, and Gregory A. Lang. 2017. Cherries: botany, production and uses, 420-430.
- Xia, Hui, Yanqiu Shen, Tian Shen, Xin Wang, Xuefeng Zhang, Peng Hu, Dong Liang, et al. "Melatonin Accumulation in Sweet Cherry and Its Influence on Fruit Quality and Antioxidant Properties." Molecules 25, no. 3 (January 2020): 753.



I am appreciative of the Summer Research program at Hobart and William Smith Colleges for introducing me to this research opportunity at USDA-ARS. I am grateful to Dr. Benjamin Gutierrez and Victoria Maekem for guiding me through this project. I am also grateful to Professor Christoph Duplais for his help with the melatonin identification.