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Metabolomic Profiling and Sensorial Quality of 'Golden Delicious', 'Liberty', 'Santana', and 'Topaz' Apples Grown Using Organic and Integrated Production Systems

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Supporting Information

ABSTRACT: Apple quality was investigated in the scab-resistant 'Liberty', 'Santana', and 'Topaz' cultivars and the scabsusceptible 'Golden Delicious' cultivar. Trees subjected to the same crop load were cultivated using either an organic (ORG) or an integrated production (IP) system. Physicochemical properties, phenolic content, and sensorial quality of fruit from both systems were compared. There were no significant differences in fruit mass, starch, and total soluble solid content (the latter was higher in ORG 'Liberty') between ORG and IP fruit, whereas significantly higher flesh firmness was found in ORG fruit (except no difference in 'Golden Delicious'). Significantly higher total phenolic content in ORG fruit was found in 'Golden Delicious', whereas differences in other cultivars were not significant. Targeted metabolomic profiling of multiple classes of phenolics confirmed the impact of the production system on the 'Golden Delicious' phenolic profile as higher levels of 4-hydroxybenzoic acid, neo- and chlorogenic acids, phloridzin, procyanidin B2+B4, -3-O-glucoside and -3-O-galactoside of quercetin, kaempferol-3-O-rutinoside, and rutin being found in ORG fruit. The results obtained suggested that scab resistance influenced the phenolic biosynthesis in relation to the agricultural system. Sensorial evaluation indicated significantly better flavor (except for 'Topaz') and better appearance of IP fruit.

KEYWORDS: apples, organic production, integrated production, scab resistance, UPLC-MS/MS, targeted metabolomic profiling, polyphenols, sensorial quality

INTRODUCTION

Fruits are the biggest source of phenolics, the most widespread plant micronutrients, important for human health and providing effective antioxidant, anti-inflammatory, vasodilatory, and prebiotic properties.¹ According to the Food and Agriculture Organization (FAO), 75.6 million tons of apples was grown worldwide in 2011.² As they are produced in such large quantities, apples are an important source of phenols, especially proanthocyanidins, in the human diet.^{3,4} The main phenolic classes in apples are flavanols (catechins and proanthocyanidins), followed by hydroxycinnamates, flavonols, dihydrochalcones, and red apple anthocyanins.^{5,6} Polyphenols have been found to be the main source of antioxidants in apples, rather than vitamin C.⁷ The main contributors to the antioxidant activity of apples have been found to be flavan-3ols/procyanidins,⁸ in terms of the five major phenolic groups, and procyanidin B2, quercetin, and epicatechin in terms of individual compounds.

Besides their importance for human health, phenols are an important factor in terms of plant resistance to pathogens, herbivores, and other biotic and abiotic stress factors.⁹ They play an important role in the resistance of apple trees to scab fungus *Venturia inaequalis*,¹⁰ which is the most widespread disease in apple-growing areas with high spring and summer rainfall. There are reports that higher contents of different flavan-3-ols, hydroxycinnamates, and flavonols has been found

in the tissue of leaves and fruit infected with V. *inaequalis* in comparison to healthy tissue.¹¹

Disease control in commercial orchards can require up to 15 fungicide treatments per year. Due to the ecological damage caused by pesticides and synthetic fertilizers, the organic (ORG) system has been adopted as an alternative to conventional or integrated production (IP). It has been evaluated that the ORG system ranks first in terms of environmental and economic sustainability, the IP system second (the most persistent pesticides excluded from use), and the conventional system last (wider list of allowed pesticides, mostly thought of as full/complete chemical plant protection).¹² Until today, apple production in Europe has mostly been managed according to IP guidelines; however, the quantity of ORG-produced apples is increasing constantly at the global level.^{13,14} The reason is consumer conviction that ORG apples contain more bioactive compounds and cause less environmental problems than IP.¹⁵ Indeed, there are reports of higher phenolic compound content in ORG-grown apples.^{16,17} It was also found that crop load per tree was inversely correlated to the phenolic content in apple fruit.¹⁸ Considering the commonly smaller yield per hectare of ORG-produced

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