

## Original Article

# Phytochemicals of foods, beverages and fruit vinegars: chemistry and health effects

Fereidoon Shahidi PhD FACS FCIC FCIFST FIAFoST FIFT FRSC, Jaime McDonald, Anoma Chandrasekara MPhil and Ying Zhong MSc

*Department of Biochemistry, Memorial University of Newfoundland, St. John's, NL, Canada*

Plant-based foods and food ingredients provide a wide range of phytochemicals and antioxidants that render their beneficial health effects through a number of mechanisms. The presence of phenolics in different plant materials and beverages depends on the source material which dictates the type and quantity present. In addition, processing of raw materials, including fermentation, may alter the chemical nature and efficacy of their phenolic constituents. While vinegar has traditionally been used for food preservation and as a seasoning, more recently, fruit vinegars with different sensory characteristics have appeared in the marketplace. In addition to acetic acid, fruit vinegars often contain citric, malic, lactic, and tartaric acids and may also include phenolics, some of which are produced as a result of fermentation. The beneficial health effects of fruit vinegars may in part be related to the process-induced changes in their phenolics and generation of new antioxidative phenolics during fermentation.

**Key Words: vinegar, phenolics, flavonoids, organic acids, health effects**

## INTRODUCTION

Fruits, vegetables, and other plant foods, contain scores of functional phytochemicals and their consumption has long been associated with physical wellbeing. Among phytochemicals with health benefit are phenolic acids, flavonoids, and other polyphenols, which have been demonstrated to exhibit positive effects on certain types of cancer,<sup>1</sup> coronary heart disease,<sup>2</sup> and various inflammatory disorders.<sup>3</sup> While the exact mechanisms of these effects are unknown, the health promoting activities of compounds involved are often attributed to their phenolic constituents and ability to act as antioxidants, among others. Therefore, preventing the formation of free radicals with deleterious health effects is important in disease risk reduction.<sup>4</sup> The antioxidant activity of a given food or food product depends on the chemical nature of the compounds present, not always their quantities, as some compounds are more effective than others.<sup>5,6</sup>

Phytochemicals in fruits and their respective wines have been extensively studied. However, very few studies have examined the fermentation process and its effect on phytochemicals in their respective vinegars. Vinegar is made via the conversion of sugars to alcohol by yeast and the further conversion of alcohol to acetic acid by bacteria. The phytochemicals present in the final products depend on the source material, which will dictate their type, quantity, and quality. Historically, vinegar has found use as a preservative and condiment, but only recently has it been considered as a potential functional food ingredient.

Various types of vinegar have also proven themselves advantageous from the perspective of human health. Vinegar consumption has been associated with diminished post-prandial glucose response following a high glycemic

load meal.<sup>7</sup> In addition, a beverage made from wine and another made from rice vinegar demonstrated antihypertensive effects in rats.<sup>8,9</sup>

Plant foods, including fruits, and their fermented products, such as wines and vinegars, render functions beyond basic nutrition. Therefore, fruit and other specialty vinegars have now been introduced to the marketplace as functional food ingredients in their own right. In this study, the total phenolic and flavonoid contents and their chemical nature of several specialty vinegars were evaluated in order to gain insight into the effects of the vinegar-making process on the functional characteristics of such vinegars. In addition, the presence of different organic acids and their type in vinegars was investigated.

## MATERIALS AND METHODS

### Materials

Plum (PV), grape (GV), rice (RV), and apple (AV) vinegars were procured from Pai Chia Chen Brewery & Foods Co., Ltd., Taiwan. The remaining samples, apple cider (ACV), raspberry wine (RWV), balsamic (BV), wine (WV), and white (AA) vinegars were purchased from a local market in St John's, NL, Canada. Vinegar samples tested were devoid of any antioxidants and their pH values ranged between 2.40 and 3.20. All vinegars were stored at room temperature for the duration of the experiments.

**Corresponding Author:** Dr F. Shahidi, Memorial University of Newfoundland, St. John's, NL, Canada, A1B 3X9  
Tel: 1-709-737-8552; Fax: 1-709-737-4000  
Email: fshahidi@mun.ca  
Manuscript received 9 September 2007. Accepted 3 December 2007.

### Antioxidant Assays

The total phenolics assay was carried out according to Singleton and Rossi<sup>10</sup> and in addition, the total flavonoid content was determined using a colorimetric assay as described by Zhishen et al.<sup>11</sup> Oxygen radical absorbance capacity (ORAC) was evaluated following the procedure of Zhong et al.<sup>12</sup> Meanwhile, evaluation of 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging capacity was carried out as described by Madhujith and Shahidi.<sup>13</sup>

### HPLC Identification of Phenolic Compounds and Organic Acids

The identification of phenolics was performed by high performance liquid chromatography according to the procedure originally described by Andlauer et al.<sup>14</sup> and Wijeratne et al.<sup>15</sup> using a reversed phase C-18 column (Agilent Technologies). Compounds were tentatively identified by conventional retention times and/or mass spectral data. Organic acids were determined using a SUPELCOGEL C-610H column (Supelco) and 0.1% phosphoric acid as the mobile phase as described by Alasalvar et al.<sup>16</sup> Organic acids were identified based on retention times of organic acid standard solutions.

### RESULTS AND DISCUSSION

Plum vinegar had the lowest pH value. Meanwhile, the acidity of the remaining vinegars was in the order of white > rice > wine > raspberry wine > balsamic > grape > apple cider > apple.

Phytochemicals found in different vinegar samples are listed in Table 1. The content of phenolics in vinegars tested was, in decreasing order, plum, balsamic, wine, grape, raspberry wine, apple, apple cider, and rice vinegars. However, the total flavonoid content in the samples was in the decreasing order of balsamic, grape, plum, wine, apple cider, raspberry wine, apple, and rice vinegars, respectively. White vinegar, which is a 5% acetic acid solution, did not contain any measurable phenols. The highest number of phenolics was present in plum vinegar, but ferulic acid, which was present in the other samples, was not detected in this vinegar. Both phenyl propanoids and benzoic acid derivatives were present in the vinegars tested. The phenolics present in the vinegars often reflected those present in the original fruits and foods. However, certain compounds identified in the vinegars tested have yet to be identified in the source material or might have been generated during fermentation due to process-induced chemical changes in the phenolics present.

With respect to the ORAC and DPPH radical scavenging capacity, the vinegars tested did not follow the same trend, possibly due to the different mechanisms involved in their scavenging of free radicals. However, vinegars which had the highest phenolic and/or flavonoid content were most effective as free radical scavengers.

In a separate study, the organic acids present in different vinegars were determined. While the reference, white vinegar, contained only acetic acid, other vinegars contained citric, lactic, malic, succinic and tartaric acids, albeit at different levels and proportions. Fumaric acid was also present in some samples. The organic acids present often reflected those present in the original source

material, but others might have been lost or generated during the fermentation process.

**Table 1.** Different classes/subclasses of phytochemicals found in vinegar samples.

Chemical Class/Subclass	Examples
Benzoic acid derivatives	Syringic acid, vanillic acid
Cinnamic acid derivatives	Ferulic acid, coumaric acid
Flavonols	Quercetin, kaempferol
Flavanols	Catechin, epicatechin
Anthocyanins	Cyanidin-3-glucoside
Stilbene	Resveratrol
Organic acids	Acetic acid, malic acid
Others	Chlorogenic acid

### ACKNOWLEDGMENTS

The plum, grape, apple and rice vinegar samples were kindly provided by the Pai Chia Chen Brewery & Foods Co., Ltd., Taiwan, to whom we are most grateful.

### AUTHOR DISCLOSURES

Fereidoon Shahidi, Jaime McDonald, Anoma Chandrasekara and Ying Zhong, no conflicts of interest.

### REFERENCES

- Birt D. Phytochemicals and cancer prevention: from epidemiology to mechanism of action. *J Am Diet Assoc.* 2006;106:20-21.
- Hertog MGL, Kromhout D, Aravinis C, Blackburn H, Fidanza F, Giampaoli S, Jansen A, Menotti A, Nedeljkovic S. Flavonoid intake and long-term risk of coronary heart disease and cancer in Seven Countries Study. *Arch Int Med.* 1995;155:381-386.
- Andriantsitohaina R, Andriambeloson E, Stoclet JC. Pharmacological approaches of endothelial nitric oxide-dependent vasorelaxation induced by polyphenols from plant extracts. *Meth Enzymol.* 1999;301:522-532.
- Shahidi F. Antioxidants in food and food antioxidants. *Nahrung – Food.* 2000;44:158-163.
- Shahidi F, Nacz M. Phenolics in Food and Nutraceuticals. CRC Press, Boca Raton, FL. 2004.
- Velioglu YS, Mazza G, Gao L, Oomah BD. Antioxidant activity and total phenolics in selected fruits, vegetables and grain products. *J Agric Food Chem.* 1998;46:4113-4117.
- Jonston CS, Buller AJ. Vinegar and peanut products as complementary foods to reduce postprandial glycemia. *J Am Diet Assoc.* 2005;105:1039-1042.
- Sugiyama A, Saitoh M, Takahara A, Satoh Y, Hashimoto K. Acute cardiovascular effects of a new beverage made of wine Viniegra and grape juice, assessed using an in vivo rat. *Nutr Res.* 2003;23:1291-1296.
- Kondo S, Tayama K, Tsukamoto Y, Ikeda K, Yamori Y. Antihypertensive effects of acetic acid and vinegar on spontaneously hypertensive rats. *Biosci Biotech Biochem.* 2001;65:2690-2694.
- Singleton VL, Rossi JA. Colorimetry of total phenolics and phosphomolybdic-phosphotungstic acid reagents. *Am J Enol Vitic.* 1965;16:144-158.
- Zhishen J, Mengcheng T, Jianming W. The determination of flavonoid contents in Mulberry and their scavenging effect on superoxide radicals. *Food Chem.* 1999;64:555-559.
- Zhong Y, Khan MA, Shahidi F. Compositional characteristics and antioxidant properties of fresh and processed sea cucumber (*Cucumaria frondosa*). *J Agric Food Chem.* 2007;55:1188-1192.

13. Madhujith T, Shahidi F. Optimization of the extraction of antioxidative constituents of six barley cultivars and their antioxidant properties. *J Agric Food Chem.* 2006;54:8048-8057.
14. Andlauer W, Stumpf C, Fürst P. Influence of the acetification process on phenolic compounds. *J Agric Food Chem.* 2000;48:3533-3536.
15. Wijeratne SS, Abou-Zaid MM, Shahidi F. Antioxidant polyphenols in almond and its coproducts. *J Agric Food Chem.* 2006;54:312-318.
16. Alasalvar C, Shahidi F, Liyanapathirana C, Ohshima T. Turkish tumbul hazelnut (*Corylus avellana L.*). 1 Compositional characteristics. *J Agric Food Chem.* 2003;51:3790-3796.