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Research Article

Quality of commercial wine vinegars evaluated on the basis of total polyphenol content and antioxidant properties

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Abstract

Wine vinegar derived from fruit and grain contains a certain amount of phenolic compounds which are known to possess antioxidant properties. In this paper the quality of nine samples of wine vinegar commercially available in Bangkok was evaluated according to their total polyphenol content and antioxidant capacity compared to common distilled vinegar. The total polyphenol content was expressed in gallic acid equivalent, GAE (µg/ml sample) by Folin-Cioculteu method; while the antioxidant capacities were given as equivalent concentration of ascorbic acid (AAeq), Trolox (TLeq) and BHT (BHTeq) in µg/ml sample based on the ability to scavenge DPPH radicals and H_2O_2. Results showed that all wine vinegar samples evaluated contained greater levels of GAE (80.3-973.4 µg /ml) and antioxidant strength (22-3148 µg AAeq/ml, 15-2107 µg TLeq/ml and 140-19880 µg BHTeq/ml for DPPH scavenging activity and 462-15362 µg AAeq/ml, 270-8991 µg TLeq/ml and 194-6455 µg BHTeq/ml for H_2O_2 scavenging activity) compared to distilled vinegar. Among the nine samples of wine vinegar which were derived from different sources of fruit and grain, balsamic vinegar exhibited the strongest antioxidant capacity which correlated to the highest level of GAE. In addition, the total polyphenol content and antioxidant strength were closely correlated for the set of all the samples with r = 0.8022 for TLeq in DPPH scavenging activity and r = 0.8193 for TLeq in H_2O_2 scavenging activity. A close correlation between the two methods for antioxidant measurement was also observed (r = 0.9956). Moreover, the samples with darker colour tended to possess greater antioxidant strength in correlation with the higher total polyphenol content. This finding indicated that total polyphenol content and antioxidant capacity of wine vinegar products were varied depending on the source of raw materials. However, wine vinegar would be a good source of natural antioxidants compared to distilled vinegar.

Keywords: phenolic compounds, GAE, DPPH, balsamic vinegar, Thailand.

Introduction

Vinegar is a common condiment used in many international cuisines. Generally, vinegar can be divided into three groups; distilled vinegar, wine vinegar or brew vinegar and artificial vinegar. All vinegar products are solutions containing mainly acetic acid which has been reported to possess physiological effects; including antihypertensive property [1], enhancement of glycogen repletion in liver and muscle [2] and reduction of serum cholesterol and triacylglycerols [3]. Unlike distilled and artificial vinegars, wine vinegar contains other nutrients such as carbohydrates, amino acids and peptides, vitamins and minerals and non-nutrient substances *e.g.* carotenoids, phenolic compounds and some other pigments. The composition of wine vinegar can be varied due to the different sources of raw materials they are derived from.

Polyphenols, secondary metabolites found in higher plants, have been shown to exhibit antioxidant properties, which can have protective effects on health [4]. Wine vinegars derived from fruit and grain; for example apple cider vinegar, sherry wine vinegar, balsamic vinegar and rice wine vinegar, contain a certain amount of polyphenols. Sherry wine vinegars have been reported to contain various polyphenol contents of 200-1,000 mg/L due to the different wines of origin used in vinegar production [5]. Studies have also shown the increasing trend of polyphenol content during the aging process of sherry wine vinegars [6, 7]. Plessi *et al.* [8] have also reported an occurrence of some phenolic acids in balsamic vinegar. In addition, a close correlation between polyphenol content and antioxidant power of sherry wine vinegar samples has been observed [5]. Differences in the antioxidant properties of wine vinegars fermented from red or white grape juice were attributed to their different total phenolic contents and also to other non-phenolic antioxidants present in the samples [9].

In the present paper, qualities of commercial wine vinegars available in some supermarkets in Bangkok are evaluated according to their total polyphenol content and antioxidant properties.

Materials and Methods

Materials

A sample of distilled vinegar and nine samples of wine vinegar derived from fruit and grain, including white and red wine vinegars, apple cider vinegar, cherry wine vinegar, balsamic vinegar, wine vinegar derived from champagne and from malts were purchased from supermarkets in Bangkok, Thailand. All samples were stored in a refrigerator at 5°C until used. All chemicals and solvents used were analytical grade and purchased from Sigma Chemical Co., Ltd (USA) and either Sigma Aldrich Co., Ltd (Germany) or Merck (Thailand) Co. Ltd (Thailand).

Methods

Determination of some physicochemical properties

All vinegar samples were analyzed for pH using a digital pH meter (Mettler Toledo, MP220, Germany), total soluble solids using a hand refractometer (Atago, Japan) and total acidity according to the standard AOAC methods [10].

Determination of total polyphenol content

The total polyphenol content was determined by a Folin-Ciocalteu assay according to the method described by Singleton and Lamuela-Raventos [11], using gallic acid as the standard. The total polyphenol content was expressed as gallic acid equivalent (GAE, µg/ml sample).

Determination of DPPH radical scavenging activity

DPPH-free radical scavenging capacity of the vinegar samples was evaluated according to Su and Silva [12], with slight modification. Briefly, a dose of 5.4 ml of diluted vinegar sample was pipetted into a screw-cap test tube. Then 0.6 ml of 0.8 mM of ethanolic DPPH radical solution was added. The reaction mixture was vortexed and left to stand at room temperature in the dark for 30 min. The absorbance for the sample (A_{sample}) was measured using UV-VIS spectrophotometer (Shimadzu, UV-1601, Japan) at 517 nm against ethanol blank. A control reaction ($A_{control}$) was taken after adding DPPH solution to 5.4 ml of deionized distilled water. The percent inhibition of DPPH radical of the sample was calculated according to the equation: percent inhibition of DPPH radical = $[1 - (A_{sample}/ A_{control})] \times 100$. Every sample was analyzed in triplicate and the DPPH-free radical scavenging capacity was expressed as micrograms of ascorbic acid equivalent (AAeq), Trolox equivalent (TLeq) and BHT equivalent (BHTeq) per millilitre of sample using calibration curve of the respective standards. Linearity ranges of the calibration curves were 5-35 micrograms for ascorbic acid, 5-50 micrograms for Trolox, and 40-200 micrograms for BHT.

Determination of H_2O_2 scavenging activity

H_2O_2 scavenging activity of the vinegar samples was evaluated according to the method described by Yen and Chen [13], with slight modification. Generally, an aliquot of vinegar sample (0.1-1.0 ml) was pipetted into a screw-cap test tube and deionized distilled water was added to make the total volume of 4.0 ml. Then 0.6 ml of 4.0 mM H_2O_2 solution in 0.1 M phosphate buffer pH 7.4 was added. The reaction mixture was vortexed and left to stand at room temperature for 10 min. The absorbance for the sample (A_{sample}) was measured using UV-VIS spectrophotometer (Shimadzu, UV-1601, Japan) at 230 nm against buffer blank. A control reaction ($A_{control}$) was taken after adding 0.6 ml of H_2O_2 solution to 4.0 ml of deionized distilled water. The percent inhibition of H_2O_2 of the sample was calculated according to the equation: percent inhibition of $H_2O_2 = [1 - (A_{sample}/ A_{control})] \times 100$. Every sample was analyzed in triplicate and the H_2O_2 scavenging activity was expressed as micrograms of ascorbic acid equivalent (AAeq), Trolox equivalent (TLeq) and BHT equivalent (BHTeq) per millilitre of sample using calibration curve of the respective standards. Linearity ranges of the calibration curves were 400-1,600 micrograms for ascorbic acid, 250-1,000 micrograms for Trolox, and 150-750 micrograms for BHT.

Correlation of total polyphenol content and antioxidant capacities of wine vinegars

Correlation analysis by scatter plots was used to evaluate the correlation between total polyphenol content and antioxidant capacity of each and also between the two methods of antioxidant capacity assays. The correlation coefficient in each case was determined using Microsoft Excel.

Results and Discussion

The observed colour of vinegar samples was dependent on the source of raw materials they were derived from. Among all wine vinegars investigated, balsamic vinegar was exceptionally dark in colour and about 3-4 times higher in total soluble solids content (Table 1). The pH of

all vinegar samples ranged from 2.35 to 3.15, while the total titrable acidity varied from 5.01 to 7.14 % w/v as acetic acid which was about the same as values shown on the label.

Table 1. Observed colour, total soluble solid content, pH and total titratable acidity of wine vinegar samples.

Sample	Ranking from lightest to darkest colour	Total soluble solid content (°Brix)	pH	Total titrable acidity (% w/v as acetic acid)	
				Analyzed value*	Value on the label
1. Distilled vinegar	1	0	2.69	5.40	5
2. White wine vinegar A	2	4.6	2.90	6.15	6
3. White wine vinegar B	4	4.0	2.35	6.27	-
4. Wine vinegar derived from champagne	3	4.4	2.48	7.02	7
5. Apple cider vinegar	5	4.8	3.15	5.25	5
6. Wine vinegar derived from malt	6	5.0	2.79	5.01	5
7. Red wine vinegar A	7	5.6	2.87	6.48	6
8. Red wine vinegar B	9	4.2	2.80	6.12	6
9. Cherry wine vinegar	8	4.8	2.68	7.14	7
10. Balsamic vinegar	10	18.2	3.01	6.21	-

* Values are means of three measurements with coefficient of variance less than 6%.

The total polyphenol content and antioxidant properties were analyzed for all vinegar samples and expressed as gallic acid equivalent, GAE (µg/ml sample) and as equivalent concentration of ascorbic acid (AAeq), Trolox (TLeq) and BHT (BHTeq) in µg/ml sample based on the ability to scavenge DPPH radicals and H_2O_2, respectively. The results are shown in Figures 1-3. In general, vinegar samples with darker colour tended to present a higher content of total polyphenols and antioxidant capacity. Balsamic vinegar exhibited the greatest values in both parameters evaluated. This may be due to the nature of balsamic vinegar in that it is produced from a slow acetification of concentrated white grape must with high sugar content carried out in series of wooden barrels. The long period of maturation and aging processes yield a vinegar product with high acidity, sugar and density [8].

Based on the total polyphenol contents, the wine vinegar samples in this study can be divided into three groups. Group 1 included white wine vinegar A, B and wine vinegar derived from champagne in which the content of total polyphenols was less than 100 µg/ml. Group 2 consisted of apple cider vinegar and red wine vinegar A, B with total polyphenol content ranging from 159-185 µg/ml. Group 3 contained total polyphenols higher than 400 µg/ml which included wine vinegar derived from malt, cherry wine vinegar and balsamic vinegar. Alonso *et al.* [5] reported the difference in GAE (200-1,000 µg/ml) found among sherry wine vinegar samples due to the different wines of origin used by each manufacturer. This information confirms the variation in polyphenol contents found in different samples of wine vinegars derived from various raw materials. Results also indicated that all wine vinegars exhibited higher total polyphenol content and antioxidant strength compared to common distilled vinegar.

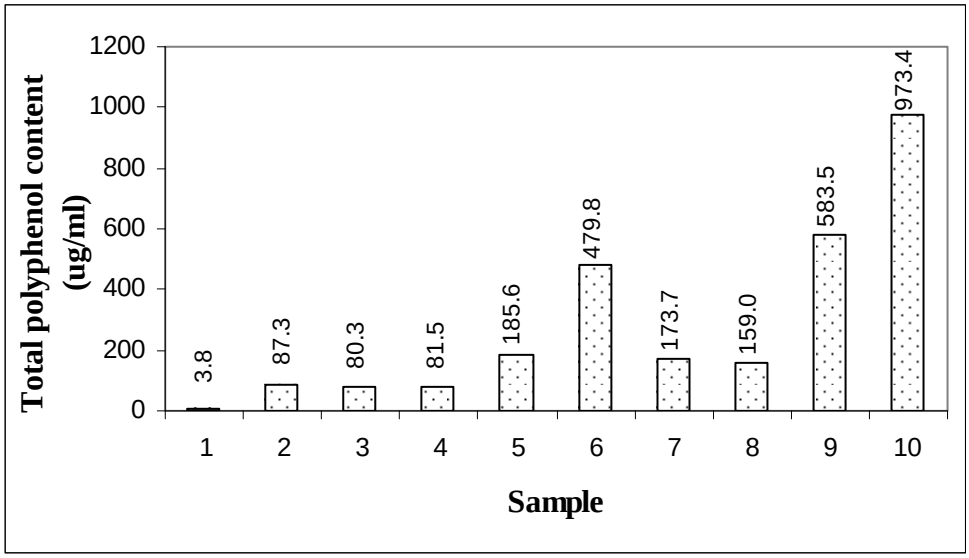

Figure 1. Total polyphenol content of wine vinegar samples.
Sample numbers correspond to the numbers in Table 1. Values are means of three measurements with coefficient of variance less than 5%.

Figures 2 and 3 compare the ability of wine vinegars to scavenge DPPH radicals and H_2O_2 with distilled vinegar. All wine vinegars presented greater capacity in H_2O_2 scavenging than in DPPH radical scavenging. A correlation analysis was made between total polyphenol content and antioxidant capacity of each, as well as between the two methods of antioxidant capacity assay (Table 2). The total polyphenol content and DPPH radical scavenging or H_2O_2 scavenging activity were closely correlated for all the vinegar samples studied (r = +0.8022 or +0.8193, respectively). A very high correlation was also observed for the two methods of antioxidant capacity assay (r = +0.9956). A close correlation between polyphenol content and antioxidant power of sherry wine vinegar samples has been reported [5]. Therefore, differences in the antioxidant properties of wine vinegars fermented from different sources of raw material can be attributable to their different total phenolic contents.

Table 2. Correlation coefficients between total polyphenol contents and antioxidant capacities and between the two methods of antioxidant assays for all vinegar samples.

Correlation factor	**Correlation coefficient** (r)
Total polyphenol content vs. DPPH radical scavenging activity (TLeq) vs. H_2O_2 scavenging activity (TLeq)	 +0.8022 +0.8193
DPPH radical scavenging activity (TLeq) vs. H_2O_2 scavenging activity (TLeq)	+0.9956

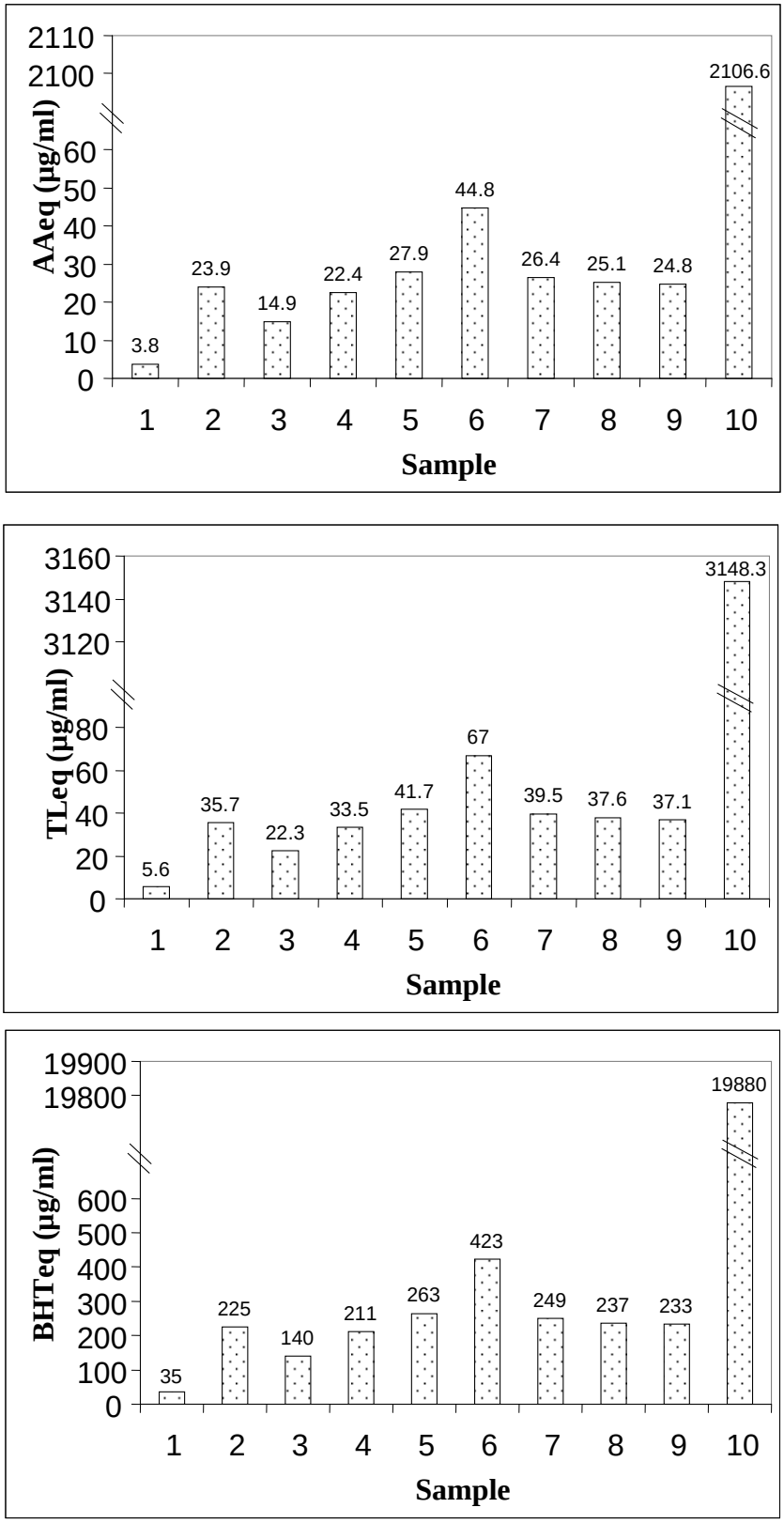

Figure 2. DPPH-free radical scavenging capacity of wine vinegar samples expressed as micrograms of ascorbic acid equivalent (AAeq), Trolox equivalent (TLeq) and BHT equivalent (BHTeq) per millilitre of sample.

Sample numbers correspond to the numbers in Table 1. Values are means of three measurements with coefficient of variance less than 6%.

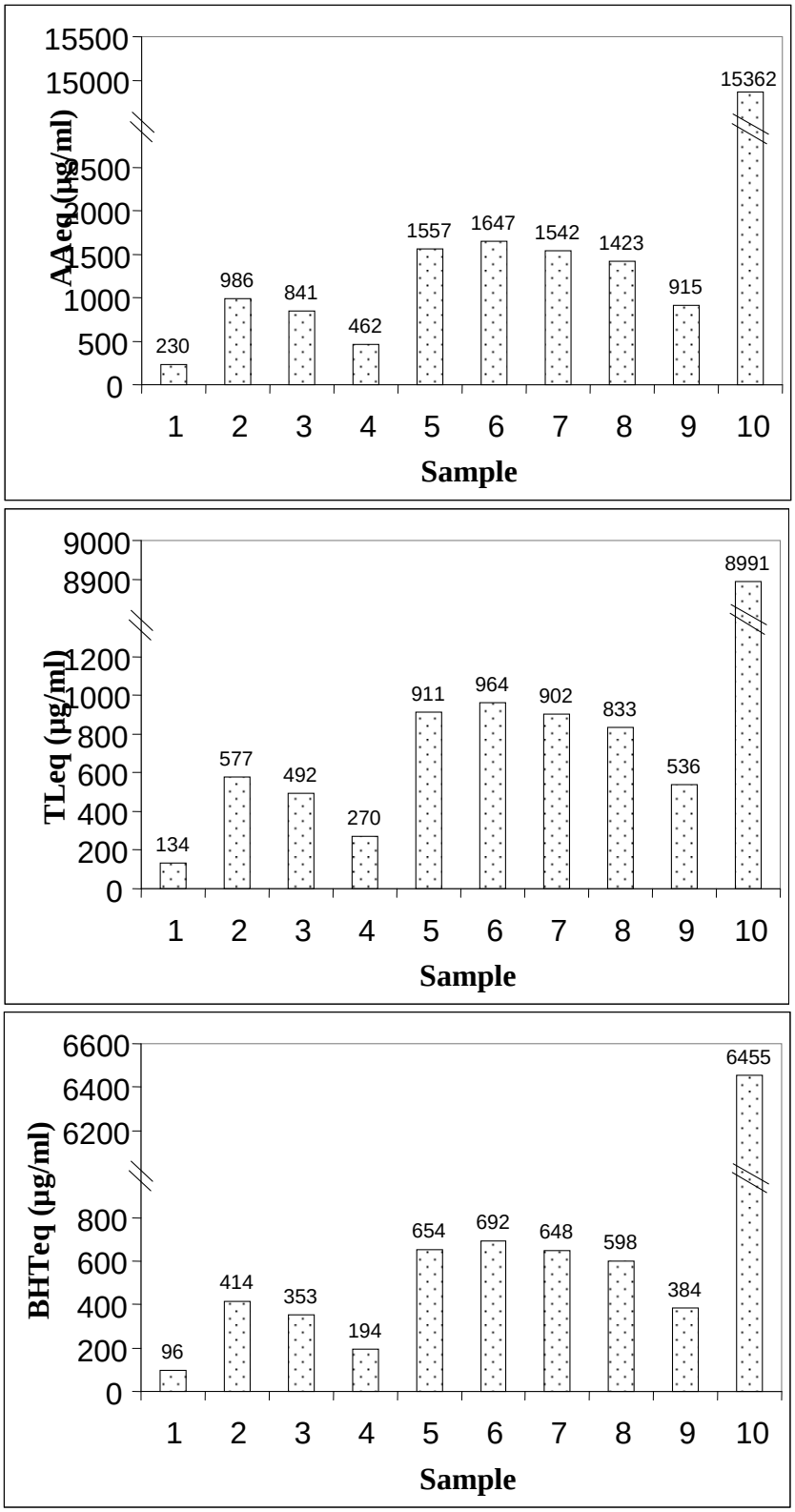

Figure 3. H_2O_2 scavenging capacity of wine vinegar samples expressed as micrograms of ascorbic acid equivalent (AAeq), Trolox equivalent (TLeq) and BHT equivalent (BHTeq) per millilitre of sample.

Sample numbers correspond to the numbers in Table 1. Values are means of three measurements with coefficient of variance less than 7%.

Conclusion

It was clear that all wine vinegar samples tested contained significantly higher total polyphenol content and possessed greater antioxidant capacity compared to distilled vinegar. Among the wine vinegars evaluated, balsamic vinegar showed the highest content of total polyphenol and antioxidant properties. The high antioxidant strength of wine vinegars were closely correlated with their high total polyphenol contents. It was concluded that most wine vinegars are a good source of natural antioxidants, especially when compared to distilled vinegar.

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