PHYSICOCHEMICAL AND ANTIOXIDANT PROPERTIES OF SELECTED POLISH GRAPE AND FRUIT WINES

Tomasz Tarko, Aleksandra Duda-Chodak, Paweł Sroka,
Paweł Satora, Elżbieta Jurasz
University of Agriculture in Krakow

Abstract. The aim of this work was to characterize the oenological profile and antioxidant properties of selected Polish grape and fruit wines. The wines produced in Golesz Vineyard in Podkarpacie and commercially available fruit wines were the experimental material. The analysed wines, except Seyval Blanc – the white grape wine, were characterized by a relatively high amount of total extract (10.5-18.8% m/v). The ethanol concentration in wines was at the similar level, only the cider, as a low-alcohol beverage, contained 5.7% (v/v) of ethanol. The red wines had the higher antioxidant potential and total polyphenol content than analyzed white grape and fruit wines. The prevailing volatile compounds of wines were higher alcohols, mainly amyl alcohols and isobutanol. The particularly high concentrations of them were detected in liqueur wines. The relatively high concentrations of propanol were also observed in the cherry wines and cider.

Key words: Polish grape wines, fruit wines, antioxidant activity, phenol compounds, volatile components

INTRODUCTION

The wine production is associated mainly with countries of moderate climate with long, hot summers. However, the vineyards are located also in countries of cooler climate. In Poland, grapevine was cultivated already in 14th century, first of all by monks for their liturgical purposes. On 20th December 2005 the Council of the European Union decided to classify Poland in wine-growing region A (the coldest), similarly to Germany, Austria and the Czech Republic. This means that wine produced in Poland can be sold in the EU market [Council Regulation... 2005]. In recent years there has been a growth of interest in grapevine and winemaking in Poland, mainly due to the emergence of new vine varieties, composed of crossbreeds better suited to the Polish climate. The increased exposure to Western European culture, growth of consumers’ knowledge about the dietetic and health properties of wine, the search for new sources
of income in Polish agriculture, and the warming of the Polish climate are also responsible for this phenomenon [Myśliwiec 2006]. According to Central Statistical Office, in 2005 there were about 2000 vineyards of a total area of 155 ha in Poland [Bosak 2006]. Since a long time, Zielona Góra, Małopolska, Sandomierz and Podkarpacie boast about their viticulture and wine production traditions [Łazarowicz 2006]. Wines produced in those regions can compete with alcoholic beverages from traditional wine countries.

There is a tradition of producing wines from fruits in Poland. Fruit winemaking in comparison with winemaking from grapes is distinguished by a high diversity of raw material that influences the must composition as well as wine production process. The final product – fruit wine – is considered as less noble than grape wine, although its quality might be very high [Jarczyk and Berdowski 1999]. The main raw material utilized for fruit wines production are apples, being the basis of national production (above 80%). For wine production the late varieties are suitable, and the fruits of average size give the product of better aroma. The chemical composition of apples and their organoleptic characteristics enable to obtain the apple wines which are light, sweet, even sparkling [Jarczyk and Berdowski 1999]. Apples, as raw material for winemaking, are utilized mainly in countries of cooler than the Mediterranean climate. In France, and to a lesser extent in England, Germany and Switzerland, so called cider apples are cultivated alongside with the dessert varieties. They are characterized by small and astringent fruits [Vidrich and Hribar 1999].

Cherries (Cerasus sp.) are one of the most important raw materials in Poland. They are very valuable for fruit wine production, chiefly because of their high content of sugars, acids, tannins, wonderful colour, and interesting taste, as well as aroma features. Besides the high sugar concentration, cherries contain vitamin C (10 mg%), A, B₂, and B₁, and large amounts of mineral compounds [Czyżowska and Pogorzelski 2003].

The raw material equally meaningful for wine production are white, black and red currants (Ribes sp.). The black currant has original and intensive fragrance, and must and wine made from them is distinguished by beautiful and intensive colour. As the currant fruit have high acid content there is a need to dilute the must [Vidrich and Hribar 1999].

For wine production, also other fruits are used: elder, cranberry, rowan, Cornelian-cherry, dog rose, sloe etc. They are also a valuable material for blending wines.

Polish grape and fruit wines, produced from native raw material, are an interesting supplement of the world wine market. The main purpose of the study was to compare the fruit and grape wines obtained from fruits cultivated in Poland. The particular attention was paid to fundamental oenological parameters and antioxidant activity of the studied wines.

MATERIAL AND METHODS

The experimental material were the Leon Millot red wine and the Seyval Blanc white wine produced in Golesz Vineyard in Podkarpacie (donated by the owners), and commercially available Polish fruit wines:

- cherry wine I – “Oryginalne” Avito S.A.,
- cherry wine II – “Cezar” TPW Vinpol Sp. z o.o.,
- fruit wine of blackberry flavour – Waldwein Bartex-Bartol s.j.,
- cider (apple wine) – Andrew’s Andy Sp. z o.o.
Chemicals

Diammonium salt of the 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic) acid (ABTS diammonium salt); (±)-6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox); a phosphate buffer saline (PBS): 0.01 M phosphate buffer, 0.0027 M potassium chloride, 0.137 M sodium chloride; pH 7.4; Folin-Ciocalteau reagent and 4-methyl-2-pentanol. All the chemicals listed, as well as GC standards, were purchased from the SIGMA-Aldrich Company (Germany). The chemicals: sodium carbonate (Na$_2$CO$_3$), potassium persulfate (K$_2$S$_2$O$_8$) and other basic chemicals were obtained from the POCh Company (Poland).

Total acidity, alcohol concentration and extract contents

Total acidity, alcohol concentration and extract contents were determined according to the International Organization of Vine and Wine [OIV... 2006].

Antioxidant activity assay

Antioxidant activity of the wines was determined according to Re et al. [1999] with slight modifications. ABTS radical was generated in the chemical reaction between the 7 mM diammonium salt of the 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic) acid and the 2.45 mM potassium persulfate. In order to terminate the reaction and to stabilize the ABTS cation-radical the solution was kept overnight in dark at ambient temperature. Prior to analysis the radical solution was diluted with phosphate buffer saline (pH 7.4) in such a way that allowed for obtaining the final absorbance of A = 0.70 ±0.02 (ABTS$_{0.7}$) measured at 734 nm.

Samples of wines (0.1 cm$^3$) or Trolox solution (conc. 1-10 mg × 100 cm$^{-3}$) were added to 1 cm$^3$ of ABTS$_{0.7}$ and the absorbance was measured 6 min after mixing. Antioxidant capacity was calculated with the use of standard curve obtained by measuring the absorbance of synthetic vitamin E solutions (Trolox) and expressed in mg of Trolox × 100 cm$^{-3}$ of wine.

Estimation of total content of polyphenols [Swain and Hillis 1959]

An amount of 45 cm$^3$ of redistilled water, 0.25 cm$^3$ of Folin-Ciocalteau reagent (water dissolved 1:1 v/v) and 0.5 cm$^3$ of 7% Na$_2$CO$_3$ were added to the 5 cm$^3$ of wine. The mixture was left for 30 min in dark. Then the absorbance was measured on a spectrophotometer (λ = 760 nm). The obtained results of total polyphenol content were expressed as mg of catechin × 100 cm$^{-3}$ of wines based on the standard plot.

Volatile compounds profile

Two milliliters of each wine sample was transferred to a 15 cm$^3$ amber vial having screw caps (Supelco) with a magnetic stirrer and 1 g of NaCl, next 0.002 cm$^3$ of internal standard (4-methyl-2-pentanol) was added. For sampling, the fiber (PDMS, 100 µm) was inserted into the headspace under magnetic stirring (300 rpm) for 35 min at 40°C. Subsequently, the SPME device (Supelco Inc., Bellefonte, PA, USA) was introduced in the injector port for chromatographic analysis and was remained in the inlet for 2 min.
The GC-SPME analysis was performed on a Hewlett Packard 5890 Series II chromatograph system. The tested components were separated on a capillary column HP-INNOVAX (crosslinked polyethylene glycol stationary phase; 30 m × 0.53 mm ID with 1.0 µm film thickness). The detector and injector temperature was 250°C, and the column was heated using the following temperature program: 35°C for five minutes at an increment 5°C × min⁻¹ to 110°C, then 40°C × min⁻¹ to 220°C and maintaining a constant temperature for three minutes. The carrier gas was helium at a 20.0 cm³ × min⁻¹ flow. Hydrogen flow speed was 33.0 cm³ × min⁻¹, and that of air – 400 cm³ × min⁻¹.

The qualitative and quantitative identification of volatile substances (acetone, ethyl acetate, propanol, isobutanol, isoamyl acetate, amyl alcohols, 2-phenylethanol) was based on the comparison of retention times and peak surface area read from sample and standard chromatograms.

Statistical analysis

There were minimum three repetitions of the whole analysis. The results were shown as an arithmetic mean (± standard deviation). A single-factor Analysis of Variance test (ANOVA) with a post hoc Tukey test was applied to assess the differences between means. A Kolmogorov-Smirnov test was applied to examine the normality of distribution.

RESULTS AND DISCUSSION

Poland is not a typical wine producing country because of the rather cold climate, but similarly to Germany and the Czech Republic, cultivation of grapevine for wine making is possible. Moreover, there is a long tradition of preparing fruit wines in Poland. The prevailing fruits in fruit wine production are apples and cherries, as well as sweet cherries, currants, and other fruits typical for Polish climate.

At the beginning of the experiments, the general characteristics of the analysed wines were considered (Table 1).

<table>
<thead>
<tr>
<th>Wines</th>
<th>Total acidity g·dm⁻³ malic acid</th>
<th>Alcohol concentration % v/v</th>
<th>Extract content % m/v</th>
</tr>
</thead>
<tbody>
<tr>
<td>Seyval Blanc</td>
<td>8.73</td>
<td>10.88</td>
<td>2.8</td>
</tr>
<tr>
<td>Leon Millot</td>
<td>5.40</td>
<td>13.41</td>
<td>10.5</td>
</tr>
<tr>
<td>Cider</td>
<td>4.73</td>
<td>5.73</td>
<td>13.2</td>
</tr>
<tr>
<td>Cherry wine I</td>
<td>4.47</td>
<td>12.8</td>
<td>12.6</td>
</tr>
<tr>
<td>Cherry wine II</td>
<td>5.14</td>
<td>13.45</td>
<td>12.7</td>
</tr>
<tr>
<td>Fruit wine</td>
<td>3.60</td>
<td>13.15</td>
<td>18.6</td>
</tr>
</tbody>
</table>
All the examined fruit wines and liqueur grape wine (Leon Millot) were characterized by a high amount of total extract. Their alcohol content was on similar level (12.8-13.5% v/v), and they can be classified as dry or semi-dry wines, according to the Polish Standard PN-A-79122 [1996]. The significantly lower alcohol concentration and amount of extract was found in the Seyval Blanc, a dry white wine. It was also shown, that cider contained the lowest ethanol content (5.7% v/v).

The titratable acidity of the analysed wines ranged from 3.6 to 8.7 g·dm$^{-3}$ of malic acid. It was shown, that fruit wines were characterized by a relatively lower acidity (3.6-5.1 g·dm$^{-3}$ malic acid). The acid concentration of fruits utilized for wine production (cherries, apples) is usually higher than that detected in grapes, but the technology of fruit winemaking involves the must dilution and extract supplementation with saccharose. The highest acid concentration was found in the Seyval Blanc wine – 8.7 g·dm$^{-3}$. Myśliwiec [2006] claims that this grapevine variety ripens reliably each year, but is distinguished by higher acids level. Therefore it requires the fermentation process that includes the lowering of the wine acidity. The obtained values of wine acidity are in accordance with Polish Standards. PN-A-79122 [1996] and PN-A-79121 [1996] define proper wine acidity in the range from 3.0 to 9.0 g·dm$^{-3}$ malic acid.

The pro-health properties of fruits and vegetables are ascribed, among other things, to the polyphenol compounds presence [Mitek and Gasik 2007]. Wine is a rich source of polyphenol compounds, mainly anthocyanins, catechins, proanthocyanidins, flavonols, and stilbens, which show potent antioxidant activity and protect cardiovascular system. The antioxidant activity and total polyphenols content of the analysed wines are shown in figure 1 and 2, respectively.

![Fig. 1. Antioxidant activity of wines. A – the same letters mean no statistically significant differences (p < 0.05)](image)

The Leon Millet red wine had the significantly higher antioxidant activity (745 mg Trolox × 100 cm$^{-3}$) compared to the others. Slight abilities to free radical scavenge were demonstrated in white grape wines and cider. It is interesting, that fruit wines demonstrated 2-fold higher antioxidant activity (233-315 mg Trolox × 100 cm$^{-3}$) than white grape wine. The antioxidant potential of wine depends mainly on polyphenols compounds. Red fruit wines were characterized by quite high concentrations of analysed compounds; at the level of red grape wine in case of fruit wine of blackberry flavour.
Although the polyphenols content in cherry wine was essentially lower than in Leon Millot grape wine, it was significantly higher compared to cider and white grape wine. Many publications [Rice-Evans et al. 1997, Owczarek et al. 2004, Przeciwnieniacze... 2007] proved that antioxidant potential of foodstuff depends mainly on quantitative and qualitative composition of polyphenols present in raw material.

One of the main factors influencing the high antioxidant activity of red grape wines is the production technology. During winemaking the grape pulp is fermented. Fruit peel and seeds are very rich in compounds with antioxidant character. The concentration of polyphenols in peel is about 10-fold higher than in the flesh [Boyer and Liu 2004, Tarko and Duda-Chodak 2007]. During intensive pressing or long contact of juice with pulp the content of phenolic compounds increases rapidly. This is connected with more efficient extraction from parts of fruit abundant in polyphenols, such as peel and seeds [Sieliwanowicz 1998]. It was found that in wines fermented with peel the concentration of antioxidant compounds had increased twice and the level of antioxidants (flavonoids, catechins, resveratrol) was up to 8 times higher [Darias-Martin et al. 2000].

Antioxidant activity and polyphenol composition were assessed in wine of Croatian origin [Katalinic et al. 2004]. The authors stated that analysed red wines were characterized by ten-fold higher antioxidant potential in comparison with white wines. The concentration of total polyphenols in white wines ranged from 300 to 400, and in red wines from 2200 to 3200 mg gallic acid per 1 L. The authors also showed that the amounts of flavonoids, catechins and anthocyanins in white wines were about 50 times lower than in red wines. Fernández-Pachón et al. [2004] examined the relationship between antioxidant activity and polyphenol composition of selected white, red and cherish wines of Spanish origin. They observed that values obtained for red wines were significantly higher than for white and cherish ones in each of the examined samples. Different techniques of antioxidant activity determination lead to discrepancies in obtained results of measurement. Antioxidant activity, described as the coefficient of ABTS and DPPH radical scavenging, was ten to fifteen times higher for red than for white wines. The total polyphenols content in red wines ranged from 1265 to 2389 mg catechin × dm$^{-3}$, whereas those values for white and cherish wines were from 200 to 400 mg·dm$^{-3}$.

Fig. 2. Total polyphenol content in wines. A – the same letters mean no statistically significant differences (p < 0.05)
Physicochemical and antioxidant properties of selected Polish grape...

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43

[Fernández-Pachón et al. 2004]. Phenolic compounds present in seeds and peel are mainly anthocyanins, hydroxycinnamic acid derivatives, flavonols and stilbenes [Passtrana-Bonilla et al. 2003]. Ten phenolic acids, both in free and conjugated forms, and 16 anthocyanin glucosides (mainly malvidin-3-glucoside) were found in fresh red grape fruits. Flavonols (mainly quercetin and kaempferol derivatives), flavanols (gallocatechin, epigallocatechin and epicatechin gallate), proanthocyanidins and condensed tannins were also detected [Szajdek and Borowska 2004]. Other research [Passtrana-Bonilla et al. 2003] showed that gallic acid, catechins and epicatechins prevailed in grape seeds, whereas in peel ellagic acid, myricetin, quercetin, kaempferol and trans-resveratrol were most common. However, those experiments did not assess the cyanic compounds. Resveratrol, belonging to the stilbenes, is a very active antioxidant. It is present in large quantities in grapes infected with Botrytis cinerea mould [Przeciwutleniacze... 2007]. In French wines the largest amount of resveratrol was present in those produced from Pinot Noir, Merlot, Gamay and Shiraz varieties. Among European wines, Swiss products are characterized by a very high level of resveratrol (above 2 times higher than in French wines) [Tarko and Duda-Chodak 2007].

Winemaking in Poland, because of available raw material, is focused mainly on fruit wines. Apples are one of the main national raw materials. According to Alonso-Salces et al. [2001] the total polyphenols content in ciders varies in wide range from 143 to 2488 mg·dm$^{-3}$. The phenolic compounds are present in the whole fruit of apple, but the highest concentrations are in peel, with large amounts of flavonols and quercetin glycosides. Phenolic acids prevailed mainly in apple flesh, while dihydrochalcons dominated in central part of fruit and seeds [Markowski and Płocharski 2006]. The phenolic compounds concentration depends both on variety and the stage of apple growth and maturity. In the Jonagold and the Elstar apple varieties, the highest concentration of quercetin glycosides, floridizin, catechins, and chlorogenic acid were found in early stages of growth, and it decreased as fruits ripen [Wzorek and Pogorzelski 1998]. In the cherry fruit the presence of flavonoids (catechin and epicatechin), phenolic acids (caftaric, vanillic, p-coumaric, caffeic, ferulic) and caffeic acid derivatives was proved [Chilla et al. 1996, Czyżowska and Pogorzelski 2003].

In the analysed wines, the content of volatile compounds, as the factors influencing taste and aroma of final product, was assayed (Table 2).

Higher alcohols are important volatile components of alcoholic beverages and – even in small amounts – play an important role in the formation of wine’s sensory characteristics. According to Vidrich and Hribar [1999] the fusels content in wine should be 80-540 mg/L. The concentration of higher alcohols below 300 mg·dm$^{-3}$ strengthens the desirable aroma of wine, whereas these components are seen as a negative factor in creating the aroma when their level exceeds 400 mg·dm$^{-3}$.

Dominating higher alcohol in the analysed grape wines were amyl alcohols and isobutanol. Among volatile compounds analysed in Spanish wines, amyl alcohols prevailed too. However, their concentration varied from 33.65 to 47.75 mg·dm$^{-3}$ [Gómez-Plaza et al. 1999]. In French wines, amyl alcohols constituted about 30% of all examined volatile compounds, and were present in amounts from 85 to 108 mg·dm$^{-3}$ [Selli et al. 2004]. Compared to these results, Polish grape wines are characterized by exceptionally high level of amyl alcohols. The content of 2-phenylethanol, the compound of mild, flowerlike aroma, in the Seyval Blanc white wine was higher than in French wines (12-16 mg·dm$^{-3}$) [Selli et al. 2004], but was about half lower than in Portuguese wines...
Table 2. Volatile compounds in wines

<table>
<thead>
<tr>
<th>Wines</th>
<th>Volatile compounds, mg·dm⁻³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>acetone</td>
</tr>
<tr>
<td>Seyval Blanc</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>±11.43</td>
</tr>
<tr>
<td>Leon Millot</td>
<td>2.02</td>
</tr>
<tr>
<td></td>
<td>±0.85</td>
</tr>
<tr>
<td>Cider</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>±0.60⁹</td>
</tr>
<tr>
<td>Cherry wine I</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>±4.56</td>
</tr>
<tr>
<td>Cherry wine II</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>±1.52⁸c</td>
</tr>
<tr>
<td>Fruit wine</td>
<td>0.00</td>
</tr>
<tr>
<td></td>
<td>±3.40⁸c</td>
</tr>
</tbody>
</table>

a, b, c – the same letters mean no statistically significant differences (p < 0.05).

(about 65 mg·dm⁻³) [Rocha et al. 2004]. It is very interesting that the Leon Millot red wine did not contain 2-phenylethanol at all, although the level of isobutanol and amyl alcohols did not vary from that of Seyval Blanc wine.

Esters play an important role in the formation of wine’s sensory characteristics. They are formed from acids and alcohols during wine fermentation and after-fermentation processes. Biosynthesis of esters mainly depends on yeast species, must aeration, fermentation technology and temperature, and fruit maturity [Roza et al. 2003]. Their amount in young wines varies over a wide range (from 25 to 300 mg·dm⁻³). The majority of esters are formed at the beginning of fermentation, and during wine maturation their concentration changes only slightly. Among wine esters very important in terms of bouquet are isoamyl acetate (banana aroma), 2-phenylethyl acetate (rose aroma), and ethyl acetate (strong, sweet aroma) [Rocha et al. 2004]. In the assessed wines, the level of isoamyl acetate was low (from 0.37 to 2.2 mg·dm⁻³), whereas ethyl acetate concentration ranged from 43 to 47 mg·dm⁻³. It should be emphasized that ethyl acetate at concentration of 150-200 mg·dm⁻³ is strongly perceptible and imposes a specific character on alcoholic beverages. At the level above 200 mg·dm⁻³ negatively influences quality of wines [Majdak et al. 2002]. The amount of ethyl acetate detected in Polish grape wines was higher than in Portuguese wines (about 35 mg·dm⁻³), but lower when compared to French products (64.1-197.2 mg·dm⁻³) [Wzorek and Pogorzelski 1998].

Similarly to grape wines, the amyl alcohols dominated in fruit wines too. The pertinent literature references available demonstrate that amyl alcohols and propanol predominate in apple wines [Satora et al. 2008]. Cider, which is produced in a different manner than typical apple wines, was characterized by lower concentration of volatile compounds. Amyl alcohols and propanol clearly prevailed, but high level of 2-phenylethanol was demonstrated. The esters concentration was many times lower than in apple wines (250 mg·dm⁻³) [Satora et al. 2008].
The analysed red fruit wines were characterized by significantly differentiated volatile composition. The cherry wine II “Cezar” contained particularly high concentrations of propanol (154 mg·dm$^{-3}$) and isoamyl acetate (2.32 mg·dm$^{-3}$); their level were several times higher than in other analysed samples. The content of ethyl acetate (133 mg·dm$^{-3}$) and isobutanol (179 mg·dm$^{-3}$) in the cherry wine I “Oryginalne” was extremely high compared with other fruit wines. Such significant diversification of results obtained for two cherry wines may denote adulteration; the admixture of cheaper raw material could be used. In relation to Polish cherry wines, the Spanish wine made from cherries had the higher concentration of ethyl acetate (183 mg·dm$^{-3}$); while the content of isobutanol (39.2 mg·dm$^{-3}$) and amyl alcohol (171-324 mg·dm$^{-3}$) was lower [Zea et al. 2001].

CONCLUSIONS

The analysed wines, except Seyval Blanc – the white grape wine, were characterized by a relatively high amount of total extract (10.5-18.8% m/v). The ethanol concentration in wines was on the similar level, only the cider, as a low-alcohol beverage, was distinguished by alcohol contents at the level of 5.7% (v/v). The red wines had the higher antioxidant potential and total polyphenol content than analysed white and fruit wines. The prevailing volatile compounds of wines were the higher alcohols, mainly amyl alcohols and isobutanol. The particularly high concentrations of them were detected in liqueur wines. The relatively high concentrations of propanol were also observed in the cherry wines and the cider.

In all analyzed Polish grape and fruit wines, the amount of total extract and alcohol content was on similar level. The red wines were characterized by higher antioxidant activity and total polyphenol content in comparison with white and fruit wines. The differences result from production technology and antioxidant potential of raw material utilized during winemaking. The prevailing volatile compounds of fruit and grape wines were amyl alcohols and isobutanol. In cherry wines and cider the relatively high concentration of propanol was also detected.

Contemporary winemaking in Poland is relatively new and requires continuous improvement and constant quality control of both raw material and wines. However, obtained fruit and grape wines, fulfil the requirements for this type of alcoholic beverages and can compete with products from other countries, especially among consumers looking for new, original tastes and aromas.

REFERENCES


Słowa kluczowe: polskie wina, wina owocowe, aktywność antyoksydacyjna, związki fenolowe, składniki lotne

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