Original Research

A Study of the UV Spectral Features in Wine and Their Correlation with Phenolic Constituents

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Abstract

Background: This study investigated the ultraviolet (UV) absorption spectra of various types and ages of grape wines and the correlation these spectra presented with their phenolic constituents. Firstly, the differences in UV spectra were characterized for different wine samples, depending on their type and age. Methods: The following methods were used in this study: ultraviolet visible spectrophotometry, Folin–Ciocalteu spectrophotometric method, high-performance liquid chromatography. Results: Then, it was demonstrated that for identically aged wines, the 280 nm absorbance is proportional to the concentration of phenolic compounds, as determined by the Folin–Ciocalteu method. Next, an investigation was conducted into the absorption coefficients of different phenolic classes commonly found in grapes and wine. Finally, the range in variation of phenolic compounds in various types of grape wines was established. Conclusions: This work provides a methodological approach to rapidly determine the concentration of phenolic compounds in wines using UV spectroscopy, provided that their age is known. As UV spectrophotometers are available in nearly all laboratories, this may provide a cheaper and faster alternative to current methods, including high-performance liquid chromatography (HPLC).

Keywords: winemaking; pomace; stems; flavanols; hydroxycinnamic acids; hydroxybenzoic acids; flavonols; anthocyanins; spectroscopy; high performance liquid chromatography (HPLC); absorption spectrum; control methods

1. Introduction

Faced with modern challenges, such as a sedentary lifestyle, increased prevalence of chronic diseases, and environmental pollution, particular attention is currently paid to the role of healthy nutrition aimed at providing the human body with the necessary nutritional components that will also have beneficial effects on its physiological activity. The most commonly consumed foods are deficient in key micronutrients such as vitamins, minerals, organic acids, antioxidants, and phenolic compounds. This can lead to impaired immune function, increased occurrence of chronic diseases, and deterioration in the quality of life. Consequently, there is a growing market demand for “functional foods” that provide health benefits and nutritional value.

Recently, there has been particular interest in polyphenols, a naturally occurring class of bio-antioxidant compounds. These act as inhibitors of free radical processes in the human antioxidant system [1], reducing cellular damage and oxidative stress. For this reason, the intake of phenolic acids has a high potential as a protective factor against cancer and cardiovascular diseases [2]. According to the US Department of Health, the daily intake of antioxidants necessary for the human body should be from 3000 to 5000 units of oxygen radical absorption capacity (ORAC)—a unit for measuring the number of antioxidants expressed in micromoles of Trolox C per unit mass (µTE/100 g) [3].

However, phenolic compounds are not endogenously synthesized in the human body, with plant foods being an almost exclusive source. Within the plant, phenolic compounds perform a similar job—preventing oxidative stress and cellular damage—alongside playing roles in filtering ultraviolet (UV) radiation and acting as internal regulatory/signaling agents. Synthesis of phenolic compounds occurs across different parts of the plant; for example, in grapes, this occurs in the stems [4], skin, and seeds of the fruit [5].

Numerous demographic studies have attempted to establish the daily intake and requirements of phenols and antioxidants in the human diet. These have shown that the average daily intake of phenolic acids in the human diet is around 200 mg/day; however, this does depend on food tastes, preferences, and diet composition [2,6,7]. The daily intake of hydroxybenzoic acids from this food for human beings is estimated to be 25–100 mg [8,9]. Hydroxycin- namic acids are generally ingested daily in high amounts, which vary significantly between individuals; an estimated intake of 153.6 to 231.8 mg/day was determined in a cross-sectional analysis of the UK National Diet and Nutrition...
Survey Rolling Programme [10]. Another study estimated the average phenolic acid consumption for men and women to be 222 mg per day, dominated by caffeic acid, with a daily intake of 206 mg [11,12]. Other work in the Netherlands has shown that the average intake of flavonols is 23 mg/day, with the proportion of quercetin being around 11.5 mg/day [13,14]. Average flavanol intake varies more widely, from 77 to 182 mg/day, and differs by geographic region [15]. According to Dutch researchers, the main bioavailable representative of flavanols is (+)-D-catechin, the mean intake of which was approximately 50 mg/day [16]. The detoxifying properties of flavanols are most pronounced in (+)-D-catechin, which inhibits the DNA damage caused by potential dietary carcinogens, such as heterocyclic amines formed from overcooking meat [17]. There is particular interest in flavonols and flavanols in the viticulture sector, as these beneficial phenolics are found in high concentrations in grapefruit and the resultant wines [18]. For this reason, there is interest in measuring the phenolic content as a quantifiable potential health benefit. Furthermore, phenolic profiles are increasingly being reported as a useful tool for quality control and authentication purposes [19]. Consequently, the viticulture industry would benefit from a rapid, non-destructive, and low-cost technique for measuring the phenolic content and profiles in grape juice and wine products.

Although the accuracy of rapid, non-destructive methods (such as spectroscopy or spectrophotometry) is typically lower than higher-end analytical techniques (such as high-performance liquid chromatography), they may be suitable for operational monitoring of the composition of wines and decision-making to adjust the technological process. This satisfies modern requirements for prompt juice and wine composition analyses at all stages throughout grape processing and wine production. The use of non-destructive methods also means no losses in the final product. In addition, there is increasing demand for integrated systems that can receive data from several different instruments, allowing for multi-parameter control of the production environment based on composition indicators and data processing algorithms [20]. With respect to measuring the phenolic composition in wine and grape products, ultraviolet (UV) spectroscopy would appear to be a suitable, non-destructive, rapid analytical technique. Phenolic compounds show distinct absorptions in the UV range, allowing for some level of identification and measurement via UV spectroscopy [21–24].

Phenolic compounds identified in grapes and subsequently transferred into wine are divided into two main classes according to their chemical structure: flavonoids (diphenylpropanoids) and non-flavonoids (phenylpropanoids). Due to their ability to enter into chemical oxidation reactions, these compounds affect the antioxidant properties of wines, their color, and taste [25]. Total phenol content can be successfully determined using UV–visible spectrophotometry by applying the Beer–Lambert law due to the dependency of absorbance on concentration and light path length [26]. Absorbance at 280 nm is frequently used to determine the total phenol content, as the aromatic rings of the phenolic compounds absorb UV light at 280 nm, causing a characteristic sharp absorbance peak at this wavelength [27]. Hydroxycinnamic acids and their derivatives can also be determined using the 320 nm absorbance [28]. Spectrophotometric detection of hydroxybenzoic acids is carried out at an absorption maximum of 219–280 nm [29]. Generally, flavonoids are characterized by two absorption maxima [30]. The presence of substituents influences the shape of the UV absorption spectrum, as does the presence of an A- or B-type ring [31]. They typically have strong absorption bands at 320–380 nm (band I) and 240–270 nm (band II). The exact position and intensity of the absorption maxima depend on further structural differences. The absorption spectra of coumarins contain two main bands at 278 and 310 nm, and in their hydroxyl derivatives, the main maximum is located above 300 nm [32]. The use of the spectrophotometric method alongside the Folin–Ciocalteu reagent in determining phenolic substances has some limitations associated with interference due to sulfur dioxide (SO₂), sugars, and ascorbic acid, which react with the Folin–Ciocalteu reagent, affecting the accuracy of the obtained total phenolic content values [28,33].

The high-performance liquid chromatography (HPLC) method exhibits high sensitivity due to the absence of restrictions on the molecular size of the identified phenolic substances [34]. HPLC coupled with a diode array detector (DAD) has successfully quantified the concentrations of various phenolic substances, with the detector programmed to record at wavelengths of 240 and 450 nm [35].

Thus, this work aimed to analyze the absorption spectra of the main types of white and red dry and fortified wines of various ages in the UV wavelength range to determine patterns in the absorption changes in the UV wavelength range depending on the type and age of the wines and to identify quantitative composition using high-performance liquid chromatography phenolic compounds, identifying the ranges of their changes in the main types of white and red wines.

2. Materials and Methods

2.1 Reagents

Spectrophotometric analysis was carried out using the Folin–Ciocalteu reagent to determine the mass concentration of phenolic substances. The Folin–Ciocalteu reagent was prepared by dissolving 100 g of sodium tungstate and 25 g of sodium molybdate in 700 mL of distilled water. Adding 50 mL of phosphoric acid 85% (ρ20 = 1.71 g/mL) and 100 mL of concentrated hydrochloric acid (ρ20 = 1.19 g/mL). Bring to the boil and reflux for 10 hours. Then, 150
g of lithium sulfate and a few drops of bromine were added, and the mixture was boiled for 15 minutes. After cooling, the solution volume was brought to 1 liter using distilled water [24].

Gallic acid, caffeic acid, malvidin-3-O-glucoside chloride, (+)-D-catechin, quercetin dihydrate, isoquercetin were purchased from Fluka Chemie (GmbH, Buchs, Switzerland), trans-resveratrol, and (−)-epicatechin, syringic acid were used as standard substances in determining the qualitative and quantitative compositions of phenolic compounds by high-performance liquid chromatography acid, p-coumaric acid, kaempferol, and ferulic acid were purchased from Sigma-Aldrich (GmbH, Munich, Germany).

2.2 Materials

The main types of white and red wines were prepared by complete or partial fermentation of pulp sugars, as well as the use of grape stems and stopping fermentation by alcoholization of various harvest years (1996–2018). A total of 215 samples were used as material in this study. Their production technology and age largely determined the choice of samples for analysis. Notably, the study included both red wines and white wines prepared by alcoholization with ethanol and must contact of the must with the solid parts of the grape bunch (grape stems and pulp), providing a complete extraction of biologically valuable compounds with a phenolic structure, and as a result, a higher extractivity of wines.

2.3 UV–Visible Spectrophotometry

High absorption values of phenolic compounds contained in wines in the UV wavelength range by light energy determine the effectiveness of spectrophotometric determination of the concentration of phenolic substances in wines of various types and ages. Before measuring the absorption rate of wines, they were diluted 15, 30, and 60 times. Considering that the maximum accuracy of measurements is achieved with absorption values of 0.3–0.7 units [36] and the maximum value of the measured absorption value should not exceed 3 units—a weakening of the radiation intensity by 1000 times, and the concentration of phenolic substances in wines is the bulk of measurements varying from 200 mg/dm³ to 1500 mg/dm³, then in a sensor that records the absorption value, the optimal optical path length should be 0.05 mm ± 0.07 mm³, the equivalent to diluting the sample 15 times. Absorption spectra were recorded in quartz cuvettes at wavelengths of 220–430 nm, with an optical path length of 1 cm after 10–20 nm, by a Specord 40 spectrometer (Analytic Jena, Jena, Germany) single-beam scanning spectrophotometer in automatic mode.

2.4 Spectrophotometric Method of Analysis Using the Folin–Ciocalteu Reagent

All phenolic substances contained in wine are oxidized by the Folin–Ciocalteu reagent. This reagent is formed from a mixture of phosphotungstic acid and phosphomolybdic acid, which, after oxidation of the phenols, is reduced to a mixture of blue oxides of tungsten and molybdenum.

The proportionality principle of the mass concentration of phenolic substances to the intensity of the absorption of the prepared reaction mixture, together with the properties of the Folin–Ciocalteu reagent that oxidizes phenolic substances, is the basis for determining the total content of phenolic compounds (TCPCs). The TCPCs were measured using the colorimetric method, as described in [24,37], with the absorbance measured using a KFK-3M spectrophotometer (GazoAnalit, Smolensk, Russia).

2.5 High-Performance Liquid Chromatography

Individual phenolic substances in the studied wine samples were determined by HPLC using an Agilent Technologies chromatographic system (model 1100) (Agilent Technologies, Waldbronn, Germany) with a diode array detector. To separate the substances, a Zorbax SB – C18 chromatographic column with a size of 2.1 × 150 mm was filled with silica gel containing a grafted octadecylsilyl phase with a sorbent particle size of 3.5 µm; chromatography was carried out in the gradient mode [37]. Mobile phase A contained methanol, while mobile phase B contained an aqueous solution of 0.6% trifluoroacetic acid. The volume of the injected sample was 10 µL. The gradient composition, reported as the proportion of mobile phase B, was programmed as follows: 0 min, 8%; 0–8 min, 8–38%; 8–24 min, 38–100%; 24–30 min, 100%. The mobile phase flow rate was 0.25 cm³/min.

Chromatograms were recorded at the following wavelengths:
- 280 nm: gallic acid, (+)-D-catechin, (−)-epicatechin
- 313 nm: derivatives of hydroxycinnamic acids
- 371 nm: quercetin
- 525 nm: anthocyanins

Individual compounds were identified by comparing their spectral characteristics with the spectra described in the literature [38–43] and by comparing the retention calibration graphs of the dependence of the peak area on the concentration of the substance, constructed from solutions of standard substances. The content of anthocyanins was determined in terms of malvidin-3-O-glucoside chloride, caftaric acid, 2-S glutathionylcaftaric acid; in terms of caffeic acid and cortaric acid; in terms of p-coumaric acid and ferratic acid; in terms of ferulic acid and quercetin-3-O-glucuronide; in terms of isoquercitrin, polymeric, and oligomeric procyanidins; in terms of (+)-D-catechin.
The mass concentrations of phenolic substances determined by HPLC were summed to determine the total concentration of the monomeric forms of the phenolic compounds (TCMFPCs).

Distilled water was used as a reference solution to dilute the wine samples. This was considered appropriate since the pH of the solution in wine samples shows little change with dilution due to the presence of buffer components in wines. All analyses were carried out in triplicate.

The measurement results were processed using standard mathematical statistical methods using the “Data Analysis” package in Microsoft Excel. The reproducibility of measurements was at least 10%, with a confidence level of $p = 0.95$.

### 3. Results and Discussion

#### 3.1 Influence of Wine Age and Phenolic Content on UV Spectra

After examining the UV spectral data, it was found that most of the studied wines had a characteristic peak within 265–285 nm (peak I), although its exact position and shape depended on their extractivity and age. The characteristic absorption spectra for the different types of wine included in this study are shown in Fig. 1.

The absorption curves analysis (Fig. 1) showed that with an increase in the extractive and age of the wine, the position of the maxima of the absorption peaks in this area shifted towards higher wavelengths, demonstrated in the inset.

### Table 1. The position of the maximum absorption in the 265–285 nm range for wines of various types and ages.

<table>
<thead>
<tr>
<th>Type of wine</th>
<th>Wine age, years</th>
<th>Peak position, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>White, dry wine</td>
<td>&lt;1</td>
<td>267 ± 2</td>
</tr>
<tr>
<td>White, dry wine</td>
<td>&gt;2</td>
<td>269 ± 2</td>
</tr>
<tr>
<td>Red, dry wine</td>
<td>&lt;1</td>
<td>277 ± 2</td>
</tr>
<tr>
<td>Red, dry wine</td>
<td>2–3</td>
<td>280 ± 2</td>
</tr>
<tr>
<td>White, fortified wine</td>
<td>1–2</td>
<td>278 ± 2.5</td>
</tr>
<tr>
<td>White, fortified wine</td>
<td>3–7</td>
<td>282 ± 2.5</td>
</tr>
<tr>
<td>White, fortified wine</td>
<td>&gt;8</td>
<td>285 ± 2.5</td>
</tr>
</tbody>
</table>

Table 1 shows the experimentally determined values of the absorption maximum for wines of various types and ages, along with their 95% confidence intervals.

The UV spectra data also demonstrated that as the age of wine increased, the shape of the peak at ca. 280 nm became less pronounced, while the absorbance in the wavelength region above 300 nm was increased. When grouped by age, there was a strong, positive correlation between the absorbance at a wavelength of 280 ± 2 nm and the concentration of the total phenolic compounds for wines of various types. This correlation is shown in Fig. 2 for young wines (1–2 years) and wines aged for 8–10 years.

Even though the peak shape of the maximum absorption of wine with aging becomes less pronounced (Fig. 1), the amount of light energy absorption at a wavelength of 280 nm per unit mass of phenolic substances increases, which can be seen in the greater slope between the pheno-
Fig. 2. Correlation between the absorbance at 280 nm (optical density $D_{280}$) by aqueous solutions of wines of various ages (diluted 30 times in water) and the total concentration of phenolic substances.

Table 2. The calculated absorption coefficients for the sum of phenolic substances found in grape products of varying ages.

<table>
<thead>
<tr>
<th>Type of wine</th>
<th>Wine age, years</th>
<th>$\varepsilon_{280}$, cm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>White, dry wine</td>
<td>1–2</td>
<td>26 ± 2</td>
</tr>
<tr>
<td>Red, dry wine</td>
<td>1–2</td>
<td>23 ± 2</td>
</tr>
<tr>
<td>White, fortified wine</td>
<td>1–2</td>
<td>26 ± 1</td>
</tr>
<tr>
<td>White, fortified wine</td>
<td>&gt;8</td>
<td>42 ± 5</td>
</tr>
</tbody>
</table>

Table 2. The calculated absorption coefficients for the sum of phenolic substances found in grape products of varying ages.

The correlation coefficient between the absorption value and the total concentration of phenolic substances was 0.98. This can be explained by the different qualitative composition of phenolic substances in young and aged wines and by the fact that, despite the degradation of anthocyanins and a decrease in the total concentration of phenolic substances during aging, grape phenolic compounds and their derivatives remain in the aged wine and show strong absorbance in the 280 nm region.

This observation suggests the use of absorbance at 280 nm as a quality indicator by measuring the concentration of total phenolic compounds in young wine materials and estimating the chemical age of the wine material (based on the slope of the absorbance/concentration curve).

3.2 Absorption Coefficients for Grape-Derived Phenolic Compounds

To generate absolute measurements of the light-absorbing ability of phenolic compounds, it is advisable to introduce the concept of the “absorption coefficient of phenolic substances of grapes and wine”. In analytical chemistry, the concept of the molar absorption (extinction) coefficient is usually used, which is equal to the absorbance of a solution with a concentration of 1 M in a cell with an optical path length of 1 cm [16]. However, because grape and wine matrices are not pure solutions and contain mixtures of various phenolic substances with various degrees of polymerization, it is necessary to use a different metric. We suggest using the absorbance of a solution at 280 nm and an optical path length of 1 cm, with the solution containing a concentration of 1 g/dm$^3$ of total phenolic substances as determined by a certified method using the Folin–Ciocalteu reagent. This indicator of phenolic substances in wine materials should be measured in the absorbance range close to 0.434 by diluting the sample with distilled water. This value was chosen empirically by preliminary experimental trials.

The obtained absorbance value should then be multiplied by the wine dilution factor and divided by the concentration of the phenolic substances. Table 2 shows the calculated values of the absorption coefficient of phenolic substances in grapes, obtained based on statistical processing of spectrophotometric data on young wine materials at a 95% confidence level.

As mentioned, the physical meaning of this value is the absorbance of a solution containing 1 g/dm$^3$ of phenolic substances determined using the Folin–Ciocalteu reagent according to the specified protocol [15], with an optical path length of 1 cm at a wavelength of 280 nm.
In this case, based on the above definition, the concentration of phenolic substances in the test sample will be equal to

\[ C = \frac{D_{280} \times n}{\varepsilon_{280}} \times 1000, \text{ mg/dm}^3 \]

where \( D_{280} \) is the absorbance of the wine material solution, measured at a wavelength of 280 nm in a quartz cell with an optical path length of 1 cm; \( n \) is the dilution factor of the wine material; \( \varepsilon_{280} \) is the absorption coefficient of phenolic substances in grapes; 1000 is the conversion factor for obtaining data in mg/dm³.

Next, we considered the possibility of directly measuring the absorbance of wines without their preliminary dilution to create a rapid sensor for calculating the concentration of phenolic substances in grapes and wine based on the absorbance at 275–280 nm. The maximum accuracy of spectrophotometric measurements is achieved at absorbance values between 0.3 and 0.7 units, and the maximum measurable absorbance value should not exceed 3 units. With respect to a 1 cm path length cuvette, this is equivalent to diluting the sample by 15 times.

### 3.3 Phenolics in Red and White Wines of Different Ages

In the next stage of the study, we investigated the qualitative and quantitative compositions of phenolic substances in the main types of white and red grape wines, from young to aged. The total concentrations of monomeric forms of phenolic substances (measured by HPLC) and the total concentration of phenolic substances (measured using the Folin–Ciocalteu method) in the main types of white grape wines are presented in Table 3, Fig. 3.

From these results (Table 3, Fig. 3), it can be seen that the average total phenolic content in the white wines ranged from 0.26 g/dm³ to 1.64 g/dm³ in dry white wines made using every component from a bunch of grapes (must, skins, seeds, and stems) for the monomeric phenolic content, the lowest value of 0.064 g/dm³ was also found for dry white wines less than 1 year old, while the highest monomeric content of 0.16 g/dm³ was identified in dry white wines made with pomace and stems. When analyzed by the proportion of phenolic substances that were monomeric forms, the lowest proportion (9.76%) was found in wines made using all components of the grape bunch (must, skins, seeds, and stems), while the highest proportion (24.10%) was seen in semi-dry and semi-sweet white wines. This difference appears to be due to the technology used in their production. The average total phenolic content in red wines ranged from 1.65 g/dm³ in dry fortified wines over 8 years old to 3.33 g/dm³ in red fortified liqueur wines aged 1–2 years (Table 4).

For the sum of the monomeric phenolic substances, the lowest content (0.12 g/dm³) was found in fortified red wines (1–2 years), and the highest (0.31 g/dm³) in dry red wines less than 1 year of age (Fig. 4).

Further investigation into the monomeric phenolic constituents in the main types of white wines revealed the presence of phenolic acids (hydroxybenzoic and hydroxycinnamic acids), flavanols, and flavonols. The highest concentration of phenolic acids (118.31 mg/dm³) was found in dry, white wines prepared using every component of the grape bunch (must, skins, seeds, and stems), while the lowest value of 30.01 mg/dm³ was found in white fortified liqueur wines over 8 years of age (Table 5).

The flavanol content varied widely, from 12.36 mg/dm³ (in white fortified liqueur wines aged 1–2 years) to 36.07 mg/dm³ (in dry white wines made using the pomace and stem). Flavonols were found in the lowest concentrations of all the monomeric phenolic substances, with contents ranging from trace amounts to 4.00 mg/dm³.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Wine description</th>
<th>Wine age, years</th>
<th>TCMFPC (measured by HPLC), g/dm³</th>
<th>TCPC (measured by Folin–Ciocalteu method), g/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>White, dry wine</td>
<td>&lt;1</td>
<td>0.06 ± 0.05</td>
<td>0.26 ± 0.08</td>
</tr>
<tr>
<td>9</td>
<td>White, aged dry wine</td>
<td>1–2</td>
<td>0.09 ± 0.04</td>
<td>0.69 ± 0.26</td>
</tr>
<tr>
<td>11</td>
<td>White, dry wine</td>
<td>&gt;2</td>
<td>0.05 ± 0.02</td>
<td>0.34 ± 0.02</td>
</tr>
<tr>
<td>15</td>
<td>White, dry wine with pomace and stems used</td>
<td>1–2</td>
<td>0.16 ± 0.05</td>
<td>1.64 ± 0.50</td>
</tr>
<tr>
<td>12</td>
<td>White, medium dry and semi-sweet wines</td>
<td>&lt;1</td>
<td>0.07 ± 0.05</td>
<td>0.29 ± 0.10</td>
</tr>
<tr>
<td>15</td>
<td>White, fortified wine</td>
<td>1–2</td>
<td>0.09 ± 0.03</td>
<td>0.63 ± 0.30</td>
</tr>
<tr>
<td>8</td>
<td>White, fortified wine</td>
<td>&gt;8</td>
<td>0.14 ± 0.07</td>
<td>0.60 ± 0.23</td>
</tr>
<tr>
<td>14</td>
<td>White, fortified liqueur wines</td>
<td>1–2</td>
<td>0.10 ± 0.04</td>
<td>0.81 ± 0.49</td>
</tr>
<tr>
<td>12</td>
<td>White, fortified liqueur wines</td>
<td>&gt;8</td>
<td>0.09 ± 0.02</td>
<td>0.71 ± 0.33</td>
</tr>
</tbody>
</table>

TCMFPC, total concentration of monomeric forms of phenolic compound; TCPC, total content of phenolic compound; HPLC, High-performance liquid chromatography.
The mass concentrations of monomeric forms of phenolic substances in the main types of white grape wines. WDW*: white dry wine, wine age <1 year; WADW: white aged dry wine, wine age 1–2 years; WDW**: white dry wine, wine age >2 years; WSDSW: white semi-dry and semi-sweet wines, wine age <1 year; WDWPS: white dry wine with the use of pomace and stems, wine age 1–2 years; WFW*: white fortified wine, wine age 1–2 years; WFW**: white fortified wine, wine age >8 years; WFLW*: white fortified liqueur wines, wine age 1–2 years; WFLW**: white fortified liqueur wines, wine age >8 years.

Table 4. The concentrations of monomeric forms of phenolic substances and the sum of phenolic substances in the main types of red grape wines (values are presented as the mean).

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Wine description</th>
<th>Wine age, years</th>
<th>TCMFPC (measured by HPLC), g/dm³</th>
<th>TCPC (measured by Folin–Ciocalteu method), g/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>Red, dry wine</td>
<td>&lt;1</td>
<td>0.31 ± 0.21</td>
<td>2.64 ± 1.20</td>
</tr>
<tr>
<td>14</td>
<td>Red, aged dry wine</td>
<td>1–2</td>
<td>0.26 ± 0.15</td>
<td>2.90 ± 1.24</td>
</tr>
<tr>
<td>10</td>
<td>Red, dry wine</td>
<td>&gt;2</td>
<td>0.24 ± 0.05</td>
<td>2.84 ± 0.67</td>
</tr>
<tr>
<td>15</td>
<td>Red, medium dry and semisweet wines</td>
<td>&lt;1</td>
<td>0.42 ± 0.20</td>
<td>2.31 ± 0.76</td>
</tr>
<tr>
<td>10</td>
<td>Red, fortified wine</td>
<td>1–2</td>
<td>0.12 ± 0.04</td>
<td>2.08 ± 1.22</td>
</tr>
<tr>
<td>12</td>
<td>Red, fortified wine</td>
<td>&gt;8</td>
<td>0.14 ± 0.04</td>
<td>1.65 ± 0.37</td>
</tr>
<tr>
<td>11</td>
<td>Red, fortified liqueur wine</td>
<td>1–2</td>
<td>0.21 ± 0.13</td>
<td>2.33 ± 1.41</td>
</tr>
<tr>
<td>10</td>
<td>Red, fortified liqueur wine</td>
<td>&gt;8</td>
<td>0.16 ± 0.05</td>
<td>1.77 ± 0.67</td>
</tr>
</tbody>
</table>

The same four classes of monomeric phenolics (hydroxybenzoic acids, hydroxycinnamic acids, flavanols, flavonols) were also found in red wines and anthocyanins (Table 6). The highest concentrations of phenolic acids (123.67 mg/dm³) were found in aged red dry wines (1–2 years of age), whereas the lowest concentrations (59.65 mg/dm³) were in red fortified liqueur wines, the age of which exceeded 8 years. The flavanol contents varied widely from 21.54 mg/dm³ (in red fortified liqueur wines over 8 years old) to 84.97 mg/dm³ (in dry red wines over 2 years old). The flavonol contents were generally higher than in white wines, with concentrations ranging...
Fig. 4. The mass concentrations of monomeric forms of phenolic substances in the main types of red grape wines. RDW*: red dry wine, wine age < 1 year; RADW: red aged dry wine, wine age 1–2 years; RDW**: red dry wine, wine age > 2 years; RSDSW: red semi-dry and semi-sweet wines, wine age < 1 year; RFW*: red fortified wine, wine age 1–2 years; RFW**: red fortified wine, wine age > 8 years; RFLW*: red fortified liqueur wines, wine age 1–2 years; RFLW**: red fortified liqueur wines, wine age > 8 years.

Table 5. The concentrations of monomeric forms of phenolic compounds in the main types of white grape wines. Values are presented as the mean. All concentrations are given as mg/dm$^3$.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Wine description</th>
<th>Wine age, years</th>
<th>Hydroxycinnamic acids</th>
<th>Hydroxybenzoic acids</th>
<th>Flavanols</th>
<th>Flavonols</th>
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<tbody>
<tr>
<td>19</td>
<td>White, dry wine</td>
<td>&lt;1</td>
<td>37.11 ± 19.82</td>
<td>3.83 ± 2.80</td>
<td>14.86 ± 11.23</td>
<td>≤1.20</td>
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<tr>
<td>9</td>
<td>White, aged dry wine</td>
<td>1–2</td>
<td>45.64 ± 17.18</td>
<td>20.79 ± 6.32</td>
<td>27.87 ± 16.78</td>
<td>≤0.88</td>
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<tr>
<td>11</td>
<td>White, dry wine</td>
<td>&gt;2</td>
<td>33.15 ± 8.30</td>
<td>7.01 ± 3.18</td>
<td>13.06 ± 7.33</td>
<td>≤0.72</td>
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<tr>
<td>15</td>
<td>White, dry wine pomace and stems used</td>
<td>1–2</td>
<td>62.56 ± 18.91</td>
<td>55.75 ± 9.97</td>
<td>36.07 ± 18.20</td>
<td>2.50 ± 0.51</td>
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<tr>
<td>12</td>
<td>White, medium dry and semisweet wines</td>
<td>&lt;1</td>
<td>39.35 ± 32.21</td>
<td>4.69 ± 2.40</td>
<td>23.96 ± 18.69</td>
<td>≤1.00</td>
</tr>
<tr>
<td>15</td>
<td>White, fortified wine</td>
<td>1–2</td>
<td>31.53 ± 18.37</td>
<td>20.93 ± 16.81</td>
<td>24.56 ± 18.26</td>
<td>4.00 ± 3.63</td>
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<tr>
<td>8</td>
<td>White, fortified wine</td>
<td>&gt;8</td>
<td>23.56 ± 15.59</td>
<td>10.62 ± 6.47</td>
<td>24.61 ± 14.59</td>
<td>1.44 ± 0.86</td>
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<tr>
<td>14</td>
<td>White, fortified liqueur wines</td>
<td>1–2</td>
<td>48.82 ± 41.61</td>
<td>12.01 ± 6.32</td>
<td>12.36 ± 8.92</td>
<td>4.59 ± 3.68</td>
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<tr>
<td>12</td>
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<td>&gt;8</td>
<td>20.98 ± 11.61</td>
<td>9.03 ± 6.88</td>
<td>21.00 ± 18.59</td>
<td>1.66 ± 0.99</td>
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</tbody>
</table>

from 1.81 mg/dm$^3$ (in red fortified liqueur wines over 8 years old) to 23.52 mg/dm$^3$ (in dry red wines aged no more than 1 year). Finally, anthocyanins, which were unique to the red wines, were found across the widest range of concentrations, from 2.13 mg/dm$^3$ (in fortified red wines over 8 years old) to 184.26 mg/dm$^3$ (in dry red wines less than 1 year old).

4. Conclusions

The study found that the UV spectra of all studied wine varieties have a characteristic absorption peak in the wavelength range of 265–285 nm, the shape of which is determined by the type and age of the wine. A strong correlation was demonstrated between the absorbance value of wine at 280 ± 2 nm and the concentration of total phenolic com-
pounds for both liqueurs and red table wines, with a correlation coefficient of 0.98. The HPLC method established the qualitative and quantitative phenolic compositions of wines of various types and ages, including monomeric forms of phenolic substances; the number of phenolic compounds; major classes of monomeric phenolic substances, including hydroxybenzoic acids, hydroxycinnamonic acids, flavonols, flavonones, and anthocyanins. These results may be used to support the authenticity and establish the quality of grape wines based on their phenolic composition.

**Availability of Data and Materials**
The dataset is available from the corresponding author upon request.

**Author Contributions**
Conceptualization, YG and MR; Methodology, RT; Software, AK and MR; Validation, JJ; Formal Analysis, YG, RT, LS; Investigation, YG; Data Curation, LS; Writing – Original Draft Preparation, YG, JJ and RT; Writing – Review and Editing, AK and MR; Project Administration, AK and MR. All authors have read and agreed to the published version of the manuscript. All authors have participated sufficiently in the work to take public responsibility for appropriate portions of the content and agreed to be accountable for all aspects of the work in ensuring that questions related to its accuracy or integrity. All authors contributed to editorial changes in the manuscript.

**Ethics Approval and Consent to Participate**
Not applicable.

**Acknowledgment**
Not applicable.

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This research received no external funding.

**Conflict of Interest**
The authors declare no conflict of interest.

<table>
<thead>
<tr>
<th>Number of samples</th>
<th>Wine description</th>
<th>Wine age, years</th>
<th>Hydroxyxycinnamic acids</th>
<th>Hydroxybenzoic acids</th>
<th>Flavanols</th>
<th>Flavanols</th>
<th>Anthocyanins</th>
</tr>
</thead>
<tbody>
<tr>
<td>18</td>
<td>Red, dry wine</td>
<td>&lt;1</td>
<td>68.24 ± 53.36</td>
<td>9.78 ± 19.79</td>
<td>71.90 ± 66.40</td>
<td>23.52 ± 21.38</td>
<td>184.26 ± 172.70</td>
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<tr>
<td>14</td>
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<td>1–2</td>
<td>46.59 ± 35.24</td>
<td>77.08 ± 51.35</td>
<td>70.52 ± 67.34</td>
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<td>42.74 ± 40.65</td>
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<td>Red, dry wine</td>
<td>&gt;2</td>
<td>47.88 ± 24.61</td>
<td>73.22 ± 16.45</td>
<td>84.97 ± 49.29</td>
<td>12.89 ± 3.67</td>
<td>18.87 ± 7.72</td>
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<td>&lt;1</td>
<td>58.81 ± 16.62</td>
<td>41.52 ± 24.13</td>
<td>55.69 ± 22.16</td>
<td>22.30 ± 9.27</td>
<td>112.00 ± 74.88</td>
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<td>1–2</td>
<td>45.00 ± 15.14</td>
<td>33.71 ± 4.56</td>
<td>28.78 ± 14.25</td>
<td>15.96 ± 13.46</td>
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<td>12</td>
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<td>&gt;8</td>
<td>42.85 ± 15.94</td>
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<td>11</td>
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<td>72.69 ± 57.02</td>
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<td>44.92 ± 39.03</td>
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<td>28.83 ± 28.42</td>
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<tr>
<td>10</td>
<td>Red, fortified liqueur wines</td>
<td>&gt;8</td>
<td>26.89 ± 11.74</td>
<td>32.76 ± 16.05</td>
<td>21.54 ± 9.71</td>
<td>1.81 ± 1.55</td>
<td>6.23 ± 5.94</td>
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</tbody>
</table>

**References**


