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Volatile compounds responsible for aroma of Jutrzenka liquer wine

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ABSTRACT

Jutrzenka is a sweet liquer wine produced in Poland from the grape variety of the same name, developed in Poland to withstand the harsh climate of winery regions. Jutrzenka wine has a characteristic aroma with strong fruity and flowery notes, which make it unique among other liquer wines as demonstrated in sensory profile analysis. The work was aimed at characterization of volatile compounds in this wine, with the emphasis on characterization of compounds responsible for its unique aroma. Gas chromatography–olfactometry (GC–O) was applied to identify the key odorants using aroma extract dilution analysis (AEDA) approach. To facilitate free and bound terpenes and C_{13}-norisoprenoids identification solid phase extraction (SPE) was used followed by GC/MS. Among identified key odorants β-damascenone was the compound having the highest FD (4096), followed by isoamyl alcohol, 4-mercapto-4-methyl-2-pentanone (FD = 2048), methional, linalool, ethyl decanoate (FD = 1024) and ethyl hexanoate, furaneol (FD = 512). Other significant compounds were ethyl 2-methyl propanoate, ethyl 2-methylbutanoate and phenyl ethyl alcohol. Determination of odor activity values (OAV) showed the highest values for β-damascenone (566), 4-mercapto-4-methyl-2-pentanone (288) ethyl hexanoate (32) and linalool (7). Jutrzenka exhibited also a rich profile of free, and to lesser extent bound terpenes.

1. Introduction

Poland is not known as the country of wine producers; however, there is a long tradition of grapevine cultivation and wine making in certain regions, mainly western part of Poland. The other main region for wine production is south eastern part of Poland – Podkarpacie region, where small wineries are mainly localized near Jasło. The drawback for winemaking in Podkarpacie region is the severity of winters which implied the adaptation or development of grape varieties best suitable for this region and climate conditions and also works done for cross breeding resulting in some interesting varieties. The work was pioneered by Roman Myśliwiec from Golesz Wineyard in Jasło, who developed among others Jutrzenka grape variety, which is used for production of white, mainly liquer wines for over 20 years. Similar climatic problems are encountered in Slovakia, so as a result of viticulture efforts vine hybrids, such as Devin, providing interesting aroma profiles were developed for white wine production [1].

Jutrzenka is a hybrid of Seyve Villard 12-375 and Pinot Blanc. It can withstand low temperatures (down to −25 °C) and is resistant to fungal diseases (especially grey mold). It gives fruits in second half of September and its berries are 16–18 mm, yellow-green. It has an average sugar content in the must of 18–22 g/100 ml. The most prominent feature of this variety is the strong and fruity aroma.

The most characteristic wine which is being produced using this grape variety is Jutrzenka liquer wine. In production of this sweet wine must is prepared as for dry wine (preferably 20 Brix); fermentation is performed until half of sugar turns into alcohol (10 Brix). At this stage fermentation is quenched by the addition of SO_2 (20 mg pyrosulfate/100 L). Usually no additional sugar is used for sweetening the wine. Wine is transferred into a vat, where wine distillate is added to obtain final alcohol concentration of 17%. The distillate used for alcoholization is prepared from grapes and pomace of Jutrzenka and aged one year before to wine production. The main flavor characteristic of this wine is its distinct fruity and flowery aroma.

Wine volatile profile is estimated to be around 1000 compounds, and comprises compounds of different chemical classes and character, which occur in concentrations ranging from ng/L to mg/L. Their contribution to the overall wine flavor is different, depending on their odor thresholds and concentrations. White wine aroma is especially interesting, as in its formation flavor compounds originating from grapes play a crucial role for certain wines. Monoterpenes were proposed to differentiate white wines into three classes (Muscat-type, Riesling-type and Silvaner type) [2]. Very often because of high terpenes contents, white wines have prevailing floral sensory notes. For the development of terpene-related flavors in such wines hydrolysis of terpenes from glycosides

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plays an important role [3]. White wines are often produced from overripe grapes for sweet wines and this process has a long tradition in France, Italy, Germany or Hungary. Characteristic aroma of some of these white wines is influenced by the noble rot (*Botrytis cinerea*) infection of grapes. This fungus influences flavor of sweet white Sauternes wines, produced from Semillon, Sauvignon Blanc and Muscadell grapes [4]. Also wines from such cultivars as Riesling, Tokay, Gewürtztraminer of Fiano have a sensory character influenced by *Botrytis cinerea* [5]. Sweet, fortified white wines form a distinctive group of highly appreciated wines, such as Vin Doux Naturels or Sherry. Alcohol is added to the must after initial fermentation, so they contain natural sugar. The grapes, as in sherry are sun dried before fermentation. In these wines oxidative ageing is of crucial importance in the development of their characteristic flavor [6–8]. Oxidation processes during wine ageing are also crucial for the balance of aroma compounds in Madeira wines [9].

The investigation of wine volatile compounds is usually focused either on the quantitation of compounds responsible for off-odors, determination of key odorants, or profiling volatile compounds for wine classification and tracking changes in its production, storage, etc. For the analysis of wine volatiles aimed at odorant analysis various techniques are used, mainly using liquid–liquid extraction and adsorption on resins (XAD 2) or other materials used in SPE methods. A thorough review on the use of volatiles isolation from enological products based on sorption mechanisms have been published recently [10]. Other techniques such as static, dynamic headspace or solid phase microextraction (SPME) are used, especially for the isolation of free flavor compounds [11].

To select among hundreds of volatile compounds these, which are responsible for the flavor of particular wine gas chromatography–olfactometry (GC–O) is used [12]. It allows description of aroma of compounds eluting from analytical column using human nose as a detector. Although first attempts in GC–O were made in late 1960s, this technique matured in 1980s, with the development of "quantitative" methods to assess the importance of particular compound. Of many approaches to the measurement of odor intensity perceived by human in GC–O aroma extract dilution analysis (AEDA) offers an uncomplicated way to assess the importance of particular compounds in overall aroma of the product [13]. The method is based on the sniffing at olfactometry port compounds from serial dilutions of volatiles extract obtained in a non-destructive way. Concentrated extract of volatile compound is analyzed, then diluted i.e. 2, 4, 8, 16, 32, 64, etc. times, and reanalyzed every time. Dilution factor (FD) values show in which dilution a particular compound was still perceived at the olfactometry port. This approach provides an insight into the importance of particular compounds into overall aroma. For the application in wine analysis a variation of GC–O method taking into account both aroma intensity and detection frequency has been developed [14]. The other way to quantify the odor sensation and relate it with the amounts of detected compound is the concept of odor activity values (OAV), which is a ratio of the amount of detected compound to its odor threshold. This approach relates the concentration of analyzed compounds to their sensory importance.

Although many extraction methods are available for the analysis of odorants, the main prerequisite for the technique is to provide representative sample [15]. On the other hand usually several extraction techniques are applied to isolate compounds that may be hard to obtain using one extraction method. Purge and trap systems using LiChrolut EN resins as a sorbent were used for Madeira volatiles trapping, to be subsequently used for GC–O analysis [16]. Extraction of volatile compounds from wine for GC–O purposes is often performed using dichloromethane, as used for Madeira wines [17], sweet fortified wines such as VDN Riversaltes [6]. Extracts obtained using XAD 2 column, from which apolar compounds were eluted using diethyl ether were subjected to GC–O analysis of Sauternes wines [4]. For the same type of bed (XAD 2) dichloromethane was also used for extraction of volatiles from monovarietal white wines [18]. Although solvent assisted flavor evaporation (SAFE) is used in extraction of odorants from many food products, solid, liquid and pastes in wine analysis it has not been used often. The only example found was rice wine aroma compounds isolation [19]. We decided to use SAFE extraction as the extract obtained resembled strongly original Jutrzenka wine.

As Jutrzenka liquer wine volatiles and aroma compounds have never been investigated the main objectives of this work were to characterize Jutrzenka aroma using sensory profile method in comparison to other liquer/fortified wines, identify main volatile compounds present in it in a free and bound form and characterize these compounds that are key odorants of this wine using gas chromatography–olfactometry.

2. Experimental

2.1. Wine samples

Jutrzenka wine produced in Golesz Wineyard in Jasło according to procedure outlined in Section 1 in 2005 was used for all experiments. To compare the sensory (aroma) characteristics of Jutrzenka in relation to other wines of this type 7 wines classified as liquer/fortified were used in this part of the study. They were Massandra Krymwein (Ukraine, 17% (v/v) alcohol), Moscatel de Setubal (Portugal, 17% alcohol), Riversaltes (France, 16% alcohol), Leyenda Sherry Cream (Spain, 18% alcohol), Moscatel Oro (Spain, 15% alcohol), Marsala Superiore Riserva (Italy, 18% alcohol), Offley White Porto (Portugal, 19% alcohol). All these wines were purchased in wine shops in Poznań.

2.2. Reagents and standards

All reagents and standards were purchased at Sigma Aldrich, Poznań, Poland and were of GC purity. Deuterated methional (3-(methylthio)-propanal d_3) and guaiacol (2-methoxy phenol d_3) were purchased from AromaLAB AG (Freising, Germany). Isolute 500 mg C18 SPE cartridges were obtained from Biotage AB (Uppsala, Sweden).

2.3. Sensory profile analysis of Jutrzenka and other fortified wines

Sensory analyses were performed by 10 members panel experienced in descriptive analysis. A vocabulary of odor descriptors, characteristic for this type of wines was developed in initial sessions based on literature [20]. Aroma profile analyses were performed orthonasally scoring 9 odor qualities on a 10 cm linear scale anchored on both sides for the intensity of attributes ranging from "none" to "very strong". The 20 ml wine samples were presented to the panelists in 250 ml wine glasses. The results from linear scale were converted into numerical values for data analysis. Session were run in three replicates, so 30 sets of results were obtained and subjected to statistical (Principal Components Analysis, PCA) analysis. PCA was performed using ANALSENS 5000E software (CARET Sp. z o.o., Poland).

2.4. HPLC analysis of sugars and organic acids of Jutrzenka and other fortified wines.

Determination of sugars (glucose, fructose), glycerol, tartaric acid, malic acid, citric acid, succinic acid, lactic acid and acetic acid was carried out on Merck – Hitachi system consisting of autosampler (model L-7250), pump (model L-7100) and refractive index detector (model L-7490). Analyses were performed isocratically