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CARBONYL COMPOUNDS IN ARONIA SPIRITS

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Key words: carbonyl compounds, aldehydes, ketones, acetals, fruit distillates, aronia

The effect of quality of raw materials, methods of their processing, pH of mashes, and yeast strains on the concentration of carbonyl compounds in aronia distillates was determined.

Acetaldehyde dominated aliphatic carbonyl compounds that were contained in the tested samples of aronia spirits. Its concentration varied between 0.100 g and 0.330 g/L spirit 100% v/v. Crotonaldehyde was not found in the tested samples. Distillates derived from frozen aronia berries contained almost twice more acetaldehyde (0.230 g/L spirit 100% v/v) than that obtained from fresh fruits. An adjustment of pH of aronia mashes from 3.4 to 4.5 resulted in an increase in the concentration of carbonyl compounds (in particular of acetaldehyde) from 0.304 to 0.400 g/L spirit 100% v/v. Thermal processing of fruit pulp decreased the concentration of butyraldehyde and increased concentrations of valeric and isovaleric aldehydes.

Spirits produced from mashes fermented by yeast *S. bayanus* contained approximately 43% more acetaldehyde (0.330 g/L spirit 100% v/v) than that obtained from mashes fermented by mixed strains: *Burgund, Bordeaux,* and *Steinberg.*

Carbonyl compounds (aldehydes and ketones) and acetals accounted for approximately 41-53% compounds identified by GC/MS. Aronia spirits contained diethyl acetals of butyric, isovaleric, caproic, ethoxypropionic and 2-furfuryl aldehydes. Also the "mixed" acetals of acetaldehyde and ethyl, propyl, and amyl alcohols were detected.

Aronia spirits were found to contain furfural, benzaldehyde, vanillin and furan compounds, such as dihydro–3,5–dimethyl–2(3H)– furanone.

INTRODUCTION

The production of fruit spirits in Poland as components for alcoholic beverages (brandy, okovita) production is very limited and resolves a production of plum spirit. The experiments carried out at the Department of Spirit and Yeast Technology of Institute of Fermentation Technology and Microbiology of Technical University of Lodz revealed that very interesting, valuable raw material in the production of natural spirit (distillate) are aronia berries (*Aronia melanocarpa* Elliot). The optimal conditions of fermentation of aronia fruits at the presence of selected yeast guarantee the high yield of original spirit with a good flavour and taste. Distillate from aronia berries could be an excellent component for strong alcoholic beverages production [Balcerek & Szopa, 2002; 2005].

The distilled alcoholic beverages are characterised by the presence of volatile compounds which arise during fermentation, distillation and storage processes. Identification of these compounds, especially controversial group of carbonyl compounds, is very important, not only to determine the flavour characteristics of the spirits, but also to identify anomalies that are indicative of inconsistent manufacturing.

Aldehydes contained in alcoholic beverages are intermediates of two-step processes of alpha-keto acids decarboxylation to alcohols [Kłosowski & Czupryński, 1993]. Concentrations of carbonyl compounds in spirits depend on quality of raw materials, their chemical composition, and microbial contaminations. Ultimate concentrations of aldehydes and ketones are also affected by conditions of technological processes. Parameters of fermentation wort such as: pH, temperature, concentration of sugars affect efficiency of enzymatic processes embracing conversion of glucose to pyruvate, its decarboxylation to acetaldehyde and reduction of the latter to ethanol [Kłosowski & Czupryński, 1993]. Activity of enzymes involved in these bioconversions can be decreased by deficiency of certain microelements, *e.g.* magnesium. This in turn can retard fermentation and bring about accumulation of aldehydes in fermentation wort [Łączyński, 1995].

Profiles of carbonyl compounds in raw and rectified spirits derived from diverse raw materials and their impact on sensory attributes of the spirits were determined by Goj [1990a, b; 1992]. He found that carbonyl compounds containing from 1 to 4 carbon atoms in the molecule (formaldehyde, acetone and aldehydes: acetic, propionic, isobutyric) have the relatively high threshold of sensory detectability and threshold of trace perception. According to this author, both of them significantly surpass the acceptable level of their content in rectified spirits.

Aldehydes such as valeric, isovaleric, and caproic are perceptible in concentrations close to that which are typical of rectified spirits. Therefore they can deteriorate their sen-

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sory properties. Particularly disadvantageous is the presence of crotonaldehyde and acrolein which are unsaturated, highly reactive compounds and display intensive and unpleasant smell and taste [Goj, 1990b; 1992; 1998]. Also Hashizume & Samuta [1997] and Wanikawa *et al*. [2002] postulate that carbonyl compounds contained in alcoholic beverages (wine, spirits, whisky) contribute to disadvantageous sensory properties. According to other authors [Barroso *et al.,* 1996; Ledauphin *et al.,* 2003; 2004] the presence of aldehydes and ketones is characteristic of freshly distilled, immature calvados, whisky distillates, brandy and spirits. Acetaldehyde is the dominating carbonyl compound in spirits irrespective of raw material [Nykänen, 1986; Goj, 1992].

The most characteristic aromatic aldehyde of fruit spirits derived from stone fruits is benzaldehyde with an almond-like aroma. Also furfural generated by dehydration of pentoses is typical of fruit distillates. Its content in calvados [Postel *et al.,* 1983] varies between 3.5 to 8.0 mg/L spirit 100% v/v. Apart from furfural also 5-methyl-2-furfural was detected (between 0.2 and 0.4 mg/L spirit 100% v/v). The higher concentration of furfural is ascribed by some authors to longer duration of distillation.

Different concentrations of furfural in alcoholic beverages (expressed per 1 L spirit 100% v/v) that reach approximately 8 mg/L in German brandy; 29 mg/L in French cognac; 5 mg/L in French armagnacs, can result from different conditions of distillation and equipment used in this process [Postel & Adam, 1980]. Distillation in a column apparatus results in lower concentrations of furfural in spirits than processes conducted in a co-current distillation apparatus equipped with a helmet. Therefore cognacs derived by the latter method contain more furfural, above 30 mg/L spirit 100% v/v [Postel & Adam, 1990]. Concentration of furfural in the final product depends also on maturation conditions, and can be considerably affected by the type of wood used in a maturation process [Postel & Adam, 1980].

Acetals rank among important components of alcoholic beverages. They are products of condensation of aliphatic aldehydes and alcohols. Acetals contribute to aroma of numerous alcoholic beverages obtained from fruits such as wines, cognacs *etc*. Acetals are liquids characterised by a pleasant aroma. They impart delicate taste and bouquet to alcoholic beverages. In old, mature brandies, the ratio of aldehydes to acetals is close to one while immediately after sherrization concentration of aldehydes is several fold higher as compared to acetals [Rostkowska-Denmer & Wzorek, 1998]. Concentration of acetals in high quality wines approaches 0.2-0.4 g/L, while in rums and cognacs it is close to 0.4 g/L [Opolska & Drzazga, 1991]. According to Kreipe [1963], acetals soothe sharp characteristics of cognac bouquet imparted by aldehydes.

Literature provides sparse information concerning the influence of alcoholic fermentation parameters on the formation of carbonyl compounds in fruit spirits. This study was, therefore, aimed at determining the effect of conditions of aronia spirit production on qualitative and quantitative composition of carbonyl compounds in distillates. The factors taken into consideration included: the quality of raw material (fresh or frozen), methods of its processing, pH of mashes, and yeast strains.

MATERIALS AND METHODS

Material and sample preparation

Materials subjected to analyses were raw spirits (distillates) obtained by fermentation of black-berry aronia (*Aronia melanocarpa* Elliot). Samples of berries were fermented by pure yeast cultures: either by mixed strains of yeast *Saccharomyces cerevisiae*: *Burgund, Bordeaux,* and *Steinberg* or by yeast *Saccharomyces bayanus*. All these cultures were obtained from Pure Culture Collection at the Institute of Fermentation Technology and Microbiology of the Technical University of Lodz.

All fermentation processes were carried out in one fourth-technical scale. Samples of aronia berries were disintegrated and either pasteurized at 85°C for 30 min or processed at elevated pressure and temperature of 121°C for 20 min. The mashes were supplemented with $(NH_4)_2HPO_4$ (0.2 g/kg raw fruit) and inoculated with yeast (10% v/v inoculum, corresponding to approximately 3 g d.m. yeast cells/kg).

The mashes were fermented at 30°C in 40 L stainless steel tanks (equivalent to 25-30 kg fresh berries) covered with lids protecting from the aeration. The fermenting mashes were mixed every 12 h and the changes in an apparent extract were determined. This quantity is an indicator of the beginning and termination of fermentation. It was measured in the presence of ethanol. Fermentation of the majority of mashes was terminated after 7 days.

Distillation of the fermented mashes was carried out in a copper distillation apparatus equipped with a water-steam jacket. Raw spirits obtained through the first distillation (contained 20-30% v/v ethanol) were concentrated in a distillery apparatus equipped with a birectifier (dephlegmator according to Golodetz), to approximately 45% v/v ethanol prior to further assays.

Determination of aliphatic carbonyl compounds

The carbonyl compounds in aronia-spirits (as well as the standards of: formaldehyde, acetone, acetaldehyde, propionaldehyde, crotonaldehyde, butyraldehyde, isobutyraldehyde, valeraldehyde, isovaleraldehyde, capronaldehyde) were transformed into their 2,4-DNPH derivatives by mixing 8.00 mL of a solution containing 200 mg/100 mL of 2,4-dinitrophenylhydrazine with 3.0 mL of HCl, 0.5÷20.00 mL of the spirit (or standards of carbonyl compounds) and after 30 min were filled up to the volume of 100 mL. Then, threefold extraction with 5 mL of CCl_4 was carried out. The whole extract obtained (organic phase) was transferred into a test-tube and filled up to the volume of 15 mL. Samples of this extract (10-30 μL) were analysed by the HPLC technique [Goj, 1995].

The HPLC experiments were carried out using HPLC system (Watters Associates, GB) equipped with a UV detector (α=254 nm), a UK-6 sampler and LiChrosorb Si 60 (250 mm x 3 mm i.d. x 7 μm film thickness) column. Eluent: n-heptane: n-hexane: n-butyl acetate (250:156:11.4); flow rate: 1.5 mL/min.

The determination of carbonyl compounds was carried out by external standard method.

Determination of other bouquet components

Other compounds imparting taste and aroma, in particular aldehydes, ketones and acetals were quantitatively determined after extraction with n-hexane (neutral fraction). Samples of the aronia spirits tested were extracted 3 times with the same volume of n-hexane. These extracts were pooled, concentrated under reduced pressure to approximately 2 mL.

Gas chromatographic analysis was performed using a gas chromatograph Carlo-Erba Instruments type HRGC equipped with a flame ionization detector (FID) and a split/splitless injector. The separation was achieved using a capillary column with a Stabilwax stationary phase (30 m x 0.25 mm i.d. x 0.50 μm film thickness).

GC oven temperature was programmed from 60°C (30 min isotherms) to 260°C at a rate of 4.0°C/min. Nitrogen (N_2) was used as carrier gas; flow rate 1.2 mL/min. Injector temperature was 250°C, detector temperature 260°C, and injection mode split (1:50). An injection volume of 1.0 μL was used for the spirit extract.

Gas chromatographic-mass spectrometric (GC/MS) analysis was performed using a GC 8000 gas chromatograph (Fissons) coupled with an MD 800 mass spectrometer. The capillary column and analytical conditions were as mentioned above, whereas energy of ionization reached 70 eV. Identification of the components was done on the basis of retention index and the comparison of their MS spectra with reference spectra (Wiley and NIST databases). Percentage (relative) of the identified compounds was computed from GC peak area and expressed as % of total compounds identified with the GC/MS method.

Statistical analysis

Statistical analysis of results (standard deviation, analysis of variance, correlation, Student's t-test at $\alpha=0.05$) was carried out by using computer program Origin 6.0. All processes and assays were carried out in triplicate.

RESULTS AND DISCUSSION

Acetaldehyde dominated aliphatic carbonyl compounds contained in aronia distillates obtained from fresh and frozen berries that were determined by HPLC. Its concentration varied between 0.12 and 0.23 g/L spirit 100% v/v, and accounted for 34 to 51% all carbonyl substances. Spirits from frozen fruit samples contained almost twice more acetaldehyde than that from fresh aronia berries (Figure 1).

Apart from acetaldehyde, fraction of C_1-C_4 aldehydes embraced also butyraldehyde (0.031-0.046 g/L spirit 100% v/v) and isobutyraldehyde (0.060-0.077 g/L spirit 100% v/v) (Figure 1). None of the tested samples of aronia spirits contained crotonaldehyde which is not a desired component [Goj, 1992; Czupryński *et al*., 1997].

The most abundant members of the group of aldehydes containing more than 4 carbon atoms in molecules were aldehydes: valeric and isovaleric (0.050-0.084 g/L spirit 100% v/v). Concentration of capronaldehyde varied between 0.001 and 0.002 g/L spirit 100% v/v. The total concentration of aliphatic carbonyl compounds in spirits derived from fresh fruit approached 0.348 g/L spirit 100% v/v and was by approximately 23% lower than in spirits produced from frozen aronia samples (Figure 1).

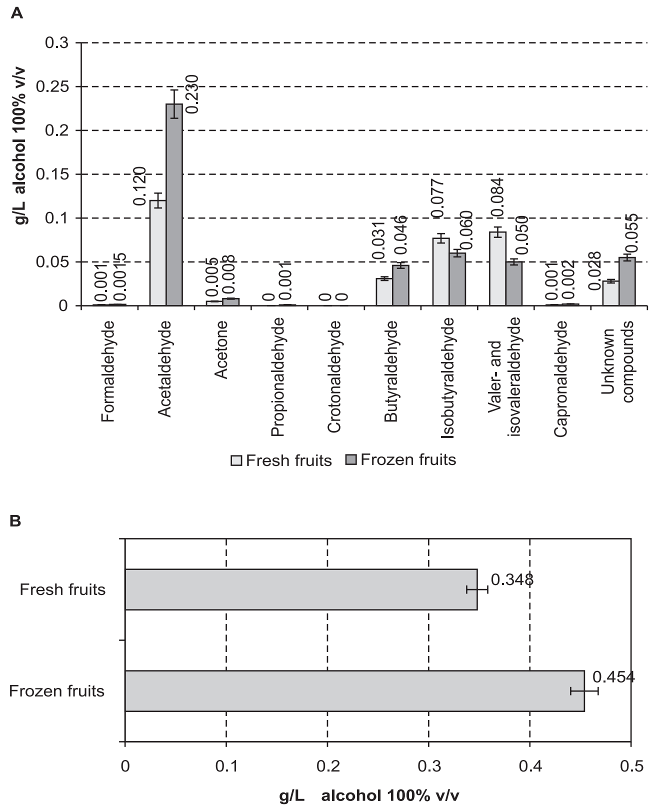

FIGURE 1. Carbonyl compounds determined by HPLC-method in aronia-spirits (A – qualitative and quantitative composition, B – sum of carbonyl compounds).

An important factor affecting the yield of synthesis of aldehydes is pH of fermentation wort [Kłosowski & Czupryński, 1993]. The lowest concentration of aldehydes (0.304 g/L spirit 100% v/v) was found in aronia spirits obtained from fermented mashes which had initial pH of 3.4 (the natural pH of aronia berries). A rise in pH of mashes to 4.5 resulted in higher concentrations of carbonyl compounds in spirits (0.400 g/L spirit 100% v/v). The concentration of acetaldehyde was considerably increased from 0.100 g to 0.158 g/L spirit 100% v/v (Table 1). The observed result can be explained by much higher activity of pyruvate decarboxylase (EC 4.1.1.1) in comparison to the activity of alcohol dehydrogenase (EC 1.1.1.1) at pH 4.5. This difference in activities could lead to the accumulation of acetaldehyde. A rise in pH of mashes from 3.4 to 4.5 caused also approximately 42% increase in the concentration of isobutyraldehyde in spirits (Table 1).

Also conditions of initial processing of aronia berries affected the concentration of aliphatic carbonyl compounds in spirits. Thermal processing at elevated temperature increased concentrations of valeric and isovaleric aldehydes. When samples of aronia berries were pasteurized (95°C, 30 min) the total concentration of the latter aldehydes reached 0.023 g/L spirit 100% v/v and was by approximately 77% higher than in distillates from fermented "raw mashes". Thermal processing at 121°C (0.1 MPa, 20 min) brought about a rise in the concentration of valeric and isovaleric aldehydes up to 0.084 g/L spirit 100% v/v. According to Kłosowski & Czupryński who cited Devreux [1993] aldehydes were generated in thermally-processed fermentation worts along with melanoidin compounds.

TABLE 1. The influence of pH and method of fruit treatment on the content of carbonyl compounds in aronia-spirits.

Method of fruit treatment	pH of mash	Content of carbonyl compounds (g/L alcohol 100% v/v)										
		Formaldehyde	Acetaldehyde	Acetone	Propionaldehyde	Crotonaldehyde	Butyraldehyde	Isobutyraldehyde	Valer- and isovaleraldehyde	Capronaldehyde	Unknown compounds	Sum
Raw pulp	3.4	0.001 ±0.0001	0.100 ±0.007	0.005 ±0.0004	0.001 ±0.0001	0.000	0.064 ±0.005	0.079 ±0.006	0.013 ±0.001	0.001 ±0.0001	0.040 ±0.003	0.304 ±0.023
	4.5	0.002 ±0.0002	0.158 ±0.011	0.003 ±0.0002	0.001 ±0.0001	0.000	0.059 ±0.004	0.112 ±0.007	0.010 ±0.0007	0.002 ±0.00015	0.053 ±0.004	0.400 ±0.027
Pasteurization (95°C, 30 min)	3.5	0.001 ±0.0001	0.110 ±0.009	0.006 ±0.0005	0.001 ±0.0001	0.000	0.026 ±0.002	0.110 ±0.008	0.023 ±0.0015	0.002 ±0.00015	0.039 ±0.003	0.318 ±0.024
Pressure-thermal treatment (121°C, 0.1 MPa, 20 min)	3.5	0.001 ±0.0001	0.102 ±0.007	0.005 ±0.0004	0.001 ±0.0001	0.000	0,031 ±0.002	0.077 ±0.006	0.084 ±0.006	0.002 ±0.00015	0.028 ±0.003	0.331 ±0.025

Mashes were obtained from fresh fruits, fermented with a mixture of yeast: *Burgund & Bordeaux & Steinberg.*

Formation of C_4 aldehydes (*e.g.* butyraldehyde) showed the opposite tendency to synthesis of C_5 aldehydes (valeric and isovaleraleric). The concentration of butyraldehyde in distillates from thermally-processed samples of aronia berries reached 0.026-0.031 g/L spirit 100% v/v and was on average 50% lower than in spirits obtained from raw mashes. None of the variants of thermal fruit processing gave rise to formation of crotonaldehyde (Table 1).

The majority of fermentation processes were conducted by using the mixture of *S. cerevisiae* strains (*Burgund, Bordeaux,* and *Steinberg*). This mixture of yeast strains was found to provide optimum yield and sensory properties of aronia spirits [Balcerek & Szopa, 2002; 2005]. For comparison, fermentation processes were also carried out by using yeast *Saccharomyces bayanus.*

The relative concentrations of carbonyl compounds in aronia spirits were almost the same irrespective of the yeast which carried out fermentation. The most abundant of these substances was acetaldehyde which accounted for 50-60% all carbonyl compounds (Table 2). However, the total concentration of carbonyl compounds in distillates from mashes fermented by *S. bayanus* approached 0.547 g/L spirit 100% v/v and was by *ca.* 22% higher as compared to that derived by using the mixed strains (Table 2). Spirits obtained from mashes fermented by *S. bayanus* contained more: formaldehyde (0.005 g/L spirit 100% v/v), acetone (0.014 g/L spirit 100% v/v), acetaldehyde (0.330 g/L spirit 100% v/v), propionaldehyde (0.004 g/L spirit 100% v/v) and capronaldehyde (0.004 g/L spirit 100% v/v) than distillates produced by using mixed strains: *Burgund, Bordeaux,* and *Steinberg*.

The brandies examined by Burini & Coli [2004] contained the concentrations of formaldehyde from 0.00204 to 0.00301 g/L which were close to the content of this compound in aronia spirit obtained from fruits fermented by the mixture of *S. cerevisiae* strains (*Burgund, Bordeaux,* and *Steinberg*).

The variations in acetaldehyde and others carbonyl compounds concentrations in aronia-spirits could by explained by differences in enzymatic capability of *S. cerevisiae* and *S. bayanus* towards their synthesis. Especially, acetaldehyde is considered to be a leakage product of the alcoholic fermentation by yeasts. There are large strain differences in acetaldehyde production by yeasts [Boulton *et al*., 1996; Henschke & Jiranek, 1993]. Acetaldehyde is excreted mainly during the growth period [Martínez *et al.,* 1997] and can be recatabolized [Farris *et al.,* 1983].

The selected samples of aronia spirits were extracted with n-hexane and the extracts were analysed by GC/MS to identify other compounds responsible for taste and aroma, in particular carbonyl compounds and acetals. Aldehydes and ketones accounted for approximately 40-52% identified substances (Table 3).

One of most abundant compounds was benzaldehyde (5.47-9.36%) which is desirable due to contributing to aroma of distillates from stone fruits and berries. This aromatic aldehyde is accumulated during alcoholic fermentation because of the concomitant hydrolysis of cyanogenic glycosides. Its

TABLE 2. The influence of yeast used for fermentation of aronia-mashes on the content of carbonyl compounds in the obtained spirits.

Strains of yeast	Content of carbonyl compounds (g/L alcohol 100% v/v)										
	Formaldehyde	Acetaldehyde	Acetone	Propionaldehyde	Crotonaldehyde	Butyraldehyde	Isobutyraldehyde	Valer- and isovaleraldehyde	Capronaldehyde	Unknown compounds	Sum
Burgund & Bordeaux & Steinberg	0.002 ±0.0002	0.230 ±0.013	0.008 ±0.0006	0.001 ±0.0001	0.000	0.046 ±0.003	0.060 ±0.004	0.050 ±0.003	0.002 ±0.0002	0.055 ±0.004	0.454 ±0.029
Saccharomyces bayanus	0.005 ±0.0004	0.330 ±0.016	0.014 ±0.001	0.004 ±0.0003	0.000	0,028 ±0.002	0.067 ±0.004	0.058 ±0.004	0.004 ±0.003	0.038 ±0.003	0.547 ±0.034

Mashes were obtained from frozen fruits, pH 3.4.

TABLE 3. Carbonyl compounds and acetals identified by GC/MS method in selected aronia-spirits.

Compound	Fresh fruits		Frozen fruits	
	Raw pulp; *Burgund & Bordeaux & Steinberg*	Pressure-thermal treatment; *Burgund & Bordeaux & Steinberg*	Pressure-thermal treatment; *Burgund & Bordeaux & Steinberg*	Pressure-thermal treatment; *Sacch. bayanus*
	% of total compounds identified with GC/MS method			
Aldehydes				
Furfural	1.35±0.10	1.89±0.15	2.20±0.20	2.32±0.20
Benzaldehyde	9.36±0.75	7.49±0.60	7.74±0.55	5.47±0.45
Vanillin	0.62±0.08	0.21±0.03	0.48±0.05	0.67±0.05
Ketones				
Pentan-2-one	0.05±0.007	0.03±0.004	0.04±0.004	0.13±0.01
Hexan-3-one	0.01±0.002	0.26±0.03	0.20±0.03	0.29±0.03
Hexan-2-one	0.03±0.005	0.34±0.04	0.26±0.03	0.46±0.05
3-Penten-2-one	0.80±0.07	0.53±0.06	0.75±0.07	0.81±0.07
Dihydro-3,5-dimethyl-2(3H)-furanone	38.91±2.20	28.66±1.15	30.41±1.15	28.86±1.14
2-ethoxy-2-phenylacetophenone	1.07±0.09	0.96±0.10	1.17±0.10	1.07±0.10
Acetals				
Butyraldehyde, diethyl acetal	0.05±0.007	0.21±0.02	0.11±0.01	0.42±0.03
Capronaldehyde, diethyl acetal	0.06±0.007	0.12±0.02	0.04±0.007	0.14±0.02
Isovaleraldehyde, diethyl acetal	0.17±0.02	0.05±0.007	0.05±0.007	0.40±0.05
2-Furaldehyde diethyl acetal	0.11±0.02	0.21±0.02	0.10±0.02	0.71±0.09
Ethoksypropionaldehyde, diethyl acetal	n.d.	n.d.	0.07±0.009	0.10±0.01
Acetaldehyde, ethyl propyl acetal	n.d.	0.14±0.02	0.03±0.005	0.11±0.02
Acetaldehyde, ethyl amyl acetal	0.20±0.03	0.11±0.02	0.20±0.03	0.61±0.05
Ethoksypropionaldehyde, diethyl acetal	n.d.	n.d.	0.07±0.009	0.10±0.01
Sum	52.79±3.32	41.21±2.27	43.85±2.30	42.59±2.37

n. d. – not detected.

presence in aronia berries was reported by Hirvi & Honkanen [1985]. Also furfural (1.35-2.32%) and low amounts of vanillin (0.21-0.67%) were found in these extracts (Table 3).

Dihydro–3,5–dimethyl–2(3H)–furanone was the most abundant ketone (29-39% all ketones). Furan compounds rank among odorants of fresh fruits and can be additionally generated during their thermal processing [Sikorski, 1996].

Other ketones contained in aronia distillates were: pentan-2-one, hexan-3-one, hexan-2-one, 3-penten-2-one and 2-ethoxy-2-phenylacetophenone. These substances are also components of freshly distilled calvadoses and cognacs [Ledauphin *et al.,* 2006].

Aronia spirits contained also diethyl acetals of such aldehydes as: butyric, isovaleric, caproic, 2-furfuryl and ethoxypropionic. Worthy of noticing are also some "mixed" acetals found in the spirits examined. They were generated through condensation of acetaldehyde with such alcohols as: ethyl, propyl, and amyl. According to Schreier [1978] these compounds are formed during distillation of natural spirits. However, the diethyl acetal of acetaldehyde was not found in any of the analysed samples.

The significant phase in synthesis of acetals is fruit spirits maturation. Balcerek & Szopa [2008] observed an increase of acetaldehyde during aronia spirits aging. The authors suppose that it is produced directly from ethanol, and its interaction with ethanol resulting in the production of acetal should be taken into consideration. According to Postel & Adam [1988], the concentration of diethyl acetal of acetaldehyde in German brandies varied between 0.04 and 0.53 g/L spirit 100% v/v. Its content in French cognacs and armagnacs was lower and ranged between 0.02 and 0.18 g/L spirit 100% v/v [Postel & Adam, 1990]. In turn, samples of Spanish brandy were rich in acetaldehyde (0.27-0.88 g/L spirit 100% v/v) and acetals (up to 0.25 g/L spirit 100% v/v) [Postel & Adam, 1996].

CONCLUSIONS

The analysis of carbonyl compounds contained in the tested aronia distillates revealed that acetaldehyde dominated among aliphatic carbonyl compounds. Its concentration depended on the quality of raw material, method of mashing, pH of the mash and a strain of yeast used in fermentation and varied between 0.10 g and 0.33 g/L spirit 100% v/v. Crotonaldehyde was not found in any of the tested spirits. Distillates derived from frozen aronia berries contained almost twice more acetaldehyde (0.23 g/L spirit 100% v/v) than that obtained from fresh fruit. An increase in pH of fruit mashes from 3.4 to 4.5 resulted in an increase in the concentration of carbonyl compounds (in particular of acetaldehyde) from 0.304 to 0.400 g/L spirit 100% v/v. Thermal processing of fruit pulp decreased the concentration of butyraldehyde and increased concentrations of valeric and isovaleric aldehydes.

Spirits produced from mashes fermented by yeast *S. bayanus* contained approximately 43% more acetaldehyde (0.33 g/L spirit 100% v/v) than that obtained from mashes fermented by mixed strains: *Burgund, Bordeaux,* and *Steinberg.*

Aronia spirits were found to contain furfural, benzaldehyde, vanillin and furan compounds, such as dihydro–3,5–dimethyl–2(3H)–furanone. They also contained diethyl acetals, and acetals of higher alcohols and acetaldehyde as well as butyric, isovaleric, caproic, 2-furfuryl and ethoxypropionic aldehydes.

REFERENCES

1. Balcerek M., Szopa J.S., Optimierung der Gewinnungstechnologie von Aronia-Spirituosen – Teil 1. Auswahl der Gärungsbedingungen für die Aronia-Maischen. Dtsch. Lebensm. Rundsch., 2002, 98, 326–331 (in German).
2. Balcerek M., Szopa J.S., Optimierung der Gewinnungstechnologie von Aronia Spirituosen Teil 2: Einfluss der Maischegärungs-Bedindungen auf die Zusammensetzung der flüchtigen Inhaltstoffe. Dtsch. Lebensm. Rundsch., 2005, 101, 16–19 (in German).
3. Balcerek M., Szopa J.S., Major volatile compounds and ethyl carbamate changes of content. Dtsch. Lebensm. Rundsch., 2008, 104, 288–292.
4. Barroso C., Rodriguez M., Guillen D., Perez-Bustamante J., Analysis of low molecular mass phenolic compounds, furfural and hydroxymethylfurfural in Brandy de Jerez by high-performance liquid chromatography –diode array detection with direct injection. J. Chrom. A., 1996, 724, 125–129.
5. Boulton R.B., Singleton V.L., Bisson L.F., Kunkee R.E., Principles and practices of winemaking. 1996, New York: Chapman & Hall, pp. 136–137, 448–473.
6. Burini G., Coli R., Determination of formaldehyde in spirits by high-performance liquid chromatography with diode-array detection after derivatization. Anal. Chim. Acta, 2004, 511 155–158.
7. Czupryński B., Kłosowski G., Kotarska K., Carbonyl compounds in raw spirits. Przem. Ferm. Owoc. Warz., 1997, 41, 14–16 (in Polish).
8. Farris G.A., Fatichenti F., Deiana P., Madau G., Functional selection of low sulfur dioxideacceptor producers among 30 *Saccharomyces cerevisiae* strains. J. Ferm. Technol., 1983, 61, 201–204.
9. Goj T., Carbonyl compounds in raw and rectified spirits derived from various raw materials and their impact on sensory properties, part 1. Carbonyl compounds in raw spirits. Przem. Ferm. Owoc. Warz., 1990a, 34, 6–8 (in Polish).
10. Goj T., Carbonyl compounds in raw and rectified spirits derived from various raw materials and their impact on sensory properties, part 2. Carbonyl compounds in rectified spirits. Przem. Ferm. Owoc. Warz., 1990b, 34, 10–12 (in Polish).
11. Goj T., Dominating carbonyl compounds in spirits and alcoholic beverages. Przem. Ferm. Owoc. Warz., 1992, 36, 5–7 (in Polish).
12. Goj T., Comparison of carbonyl compounds determination methods in natural vodkas and raw spirits. Unpublished materials, ZBR Polmos S. A. Konin, 1995 (in Polish).
13. Goj T. Chemical impurities contained in spirits. Przem. Ferm. Owoc. Warz., 1998, 42, 18–21 (in Polish).
14. Hashizume K., Samuta T., Green odorants of grape cluster stem and their ability to cause a wine stemmy flavor. J. Agric. Food Chem., 1997, 45, 1333–1337.
15. Henschke P.A., Jiranek V., Yeasts – metabolism of nitrogen compounds. 1993, in: Wine Microbiology and Biotechnology (ed. G.H. Fleet). Harwood Academic Publishers, Amsterdam, pp. 77–164.
16. Hirvi T., Honkanen E., Analysis of the volatile constituents of black chokeberry (*Aronia melanocarpa* Ell.). J. Sci. Food Agric., 1985, 36, 808–810.
17. Kłosowski G., Czupryński B., Reasons of formation of carbonyl compounds with particular consideration of acetaldehyde. Przem. Ferm. Owoc. Warz., 1993, 37, 8–10 (in Polish).
18. Kreipe W., Ost-West–Austausch von Whisky und Wodka. Die Branntweinwirtschaft, 1963, 103, 439–441.
19. Ledauphin J., Guichard H., Sain-Clair J.F., Picoche B., Barillier D., Chemical and sensorial aroma characterization of freshly distilled calvados. 2. Identification of volatile compounds and key odorants. J. Agric. Food Chem., 2003, 51, 433–442.
20. Ledauphin J., Sain-Clair J.F., Lablanquié O., Guichard H., Fournier N., Guichard E., Barillier D., Identification of trace volatile compounds in freshly distilled calvados and cognac using preparative separations coupled with gas chromatography – mass spectrometry. J. Agric. Food Chem., 2004, 52, 5124–5134.
21. Ledauphin J., Basset B., Cohen S., Payot T., Barillier D., Identification of trace volatile compounds in freshly distilled Calvados and Cognac: Carbonyl and sulphur compounds. J. Food Comp. Anal., 2006, 19, 28–40.
22. Łączyński B., Reasons of too high concentration of aldehydes in raw spirits and methods of prevention in agricultural distilleries. Przem. Ferm. Owoc. Warz., 1995, 39, 13–14 (in Polish).
23. Martínez P., Pérez Rodríguez L., Benítez T., Evolution of flor yeast population during the biological aging of fino sherry wine. Amer. J. Enol. Viticult., 1997, 48, 160–168.
24. Nykänen I., Formation and occurrence of flavor compounds in wine and distilled alcoholic beverages. Amer. J. Enol. Viticult., 1986, 37, 84–96.
25. Opolska G., Drzazga B., Characteristics of odorants in fruit distillates and their formation. Przem. Ferm. Owoc. Warz., 1991, 35, 12–13, 16 (in Polish).
26. Postel W., Adam L., Gaschromatographische Charakterisierung von Weinbrand, Cognac und Armagnac II. Mitteilung: Gehalte an flüchtigen Inhaltstoffen. Die Branntweinwirtschaft, 1980, 121, 154–163 (in German).
27. Postel W., Adam L., Jäger K.-H., Gaschromatographische Charakterisierung von Calvados. Die Branntweinwirtschaft, 1983, 124, 414–419 (in German).
28. Postel W., Adam L., Flüchtige Stoffe in deutschen Weinbränden II. Mitteilung: Carbonylverbindungen, Acetale und Terpene. Die Branntweinwirtschaft, 1988, 129, 82–85 (in German).
29. Postel W., Adam, L., Gaschromatographische Charakterisierung von Cognac und Armagnac – Gehalte an flüchtigen Verbindungen. Die Branntweinwirtschaft, 1990, 131, 208–213 (in German).
30. Postel W., Adam L., Analytische Charakterisierung spanischer Brandies. Dtsch. Lebensm. Rundsch., 1996, 82, 4–10 (in German).

31. Rostkowska-Denmer E., Wzorek W., Biochemical changes in wine composition during the process of cherring. Przem. Ferm. Owoc. Warz., 1998, 42, 34–38 (in Polish).
32. Schreier P., Drawert F., Schmid M., Changes in the composition of neutral volatile components during the production of apple brandy. J. Sci. Food Agric., 1978, 50, 728–736.
33. Sikorski Z., Chemical and functional properties of food components. 1996, WNT, Warszawa, pp. 430–436 (in Polish).
34. Wanikawa A., Hosoi K., Kato T., Nakagawa K.I., Identification of Greek note compounds in malt whisky using multidimensional gas chromatography. Flavour Fragr. J., 2002, 17, 2007–2011.

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