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# The effect of distillation conditions and alcohol content in 'heart' fractions on the concentration of aroma volatiles and undesirable compounds in plum brandies

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**This study investigates the effect of double- or single-stage distillation and different alcohol content in 'hearts' (middle fractions) on the distribution of aroma volatiles and undesirable compounds (methanol, hydrocyanic acid, ethyl carbamate) during distillation of plum brandies. Irrespective of the distillation method used, the first fractions ('heads') included mainly aliphatic aldehydes, acetals and esters as well as higher alcohols (1-propanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1-butanol and 3-methyl-1-butanol). Furfural, 1-hexanol, benzyl alcohol, 2-phenylethanol and ethyl carbamate occurred in relatively high concentrations in the 'tail' fractions. Increasing the concentration of alcohol in the heart fractions from 70 to 90% *v*/v resulted in a gradual decrease in the concentration of all detected volatile compounds. Compared with single-stage distillation, double distillation produced heart fractions with lower concentration of acetaldehyde and benzaldehyde and with higher contents of furfural and esters, such as isobutyl acetate and isoamyl acetate. There was a statistically significant increase in the amounts of methanol and ethyl carbamate obtained from double distillation compared with similar fractions derived from the single-stage process. However, in all fractions these compounds occurred in concentrations much lower than the limits specified by EU regulations. The heart fraction from the double-stage process with 83% *v*/v alcohol content received the best scores for aroma and flavour.** 

**Keywords:** plum brandy; distillation; aroma compounds; methanol; hydrocyanic acid; ethyl carbamate

## Introduction

Plum brandy (slivovitz) is a popular spirit in Eastern and Central Europe. Poland has a long tradition of producing slivovitz. One of the most recognizable types of slivovitz is Śliwowica Łącka, produced in a sub-mountainous region of Poland with specific climatic and soil conditions by spontaneous fermentation of Węgierka Zwykła plums *(1,2)*.

Slivovitz production generally consists of the following steps: fruit preparation (mashing), fermentation by indigenous microflora present on the plums or with a pure culture of wine yeast, distillation and finally maturation. To prepare the mashes for fermentation, the stoned plums are homogenized into pulp. Comminuted stones are added to the plum pulp in quantities of up to 10% by weight to obtain the 'bitter almond' taste desired by consumers *(3)*.

Two types of distillation equipment are commonly used for the production of fruit-brandy: copper Charentais alembic (French style) stills and batch distillation columns (German style) *(4,5)*. In traditional pot distillation using copper alembic stills, only limited modification of the composition of the distillate is possible during the distillation process *(6)*. Alembic stills have no trays or appreciable reflux and require multiple distillations to achieve high-proof spirits. A more flexible system is the batch distillation column, in which reflux rates may be varied over a wide range. High proofs can be achieved with a single pass through this type of still *(7)*. A third option is the use of a boiler coupled with a rectification column, equipped with an internal partial condenser. This system enables rapid control of the reflux rate in the column by manipulating the cooling flow rate *(6)*.

Fruit distillates should meet the requirements for concentrations of ethanol and other volatile compounds. According to Regulation (EC) no. 110 (2008) *(8)* of the European Parliament and the Council, fruit spirit should be distilled at $<$86% *v*/v, while the quantity of volatile substances should be $\geq$200 g/hL of alcohol 100% *v*/v. While the content of volatile compounds determines the organoleptic characteristics of fruit distillates, it is also important to limit the content of compounds such as methanol, hydrocyanic acid (HCN) and ethyl carbamate (EC), which may be harmful to human health.

Methanol is liberated from pectic substances by enzymatic degradation under the influence of a specific pectolytic enzyme, pectin methylesterase, and is subject to restrictive controls owing to its high toxicity *(9,10)*. Nonetheless, a certain amount of this compound is permitted in brandies, as a natural component of plants and fruits *(11)*. According to EU Regulation (EC) no.

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110/2008 *(8)*, the concentration of methanol in plum distillates should not exceed 12 g/L of alcohol 100% *v*/v.

Degradation of commonly occurring glycosides from *Prunus* sp., prunasin and amygdalin, leads to the liberation of benzaldehyde and HCN. Benzaldehyde is approved as a flavouring by the European Food Safety Authority *(12)*, whereas the maximum level of HCN in foodstuffs and beverages is strictly limited because of its toxicity. EU regulation (EC) no. 110 (2008) *(8)* stipulates that the HCN content in stone fruit spirits and stone fruit marc spirits should not exceed 7 g/hL of alcohol 100% *v*/v.

The maximum level of HCN in beverages is strictly limited, as it is a precursor of EC, a suspected carcinogen *(13)*. Cyanate, resulting from oxidation of HCN, reacts with ethanol to form EC *(14)*. In 2005, the Joint Food and Agriculture Organization/World Health Organization Expert Committee on Food Additive concluded that the intake of EC from foods excluding alcoholic beverages was of low concern. However, when both alcoholic beverages and fermented foods are combined, intake increases around 4-fold, and there is increased carcinogenic risk *(15)*. In 2007, the International Agency for Research on Cancer (IARC) classified EC as probably carcinogenic to humans (Group 2A) *(16)*.

Our research set out to evaluate the distribution of volatile compounds responsible for aroma and taste in Węgierka Zwykła plum distillates. We also tested the impact of distillation method and final alcohol concentrations in the heart fractions on the presence of undesirable compounds, such as methanol, HCN and EC. Assessment was focused on finding the alcohol concentration in the main (heart) fractions that had good organoleptic characteristics and the lowest possible content of compounds harmful for human health.

## Materials and methods

### Raw materials, microorganisms and supplements

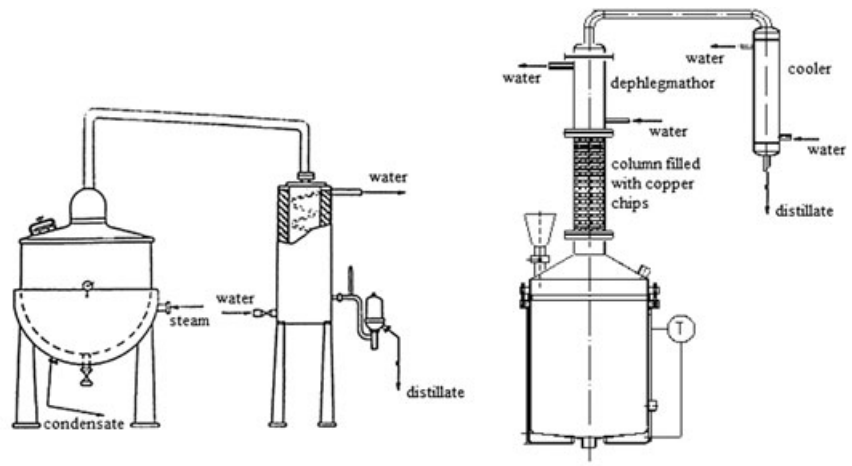
Mashes were prepared from Węgierka Zwykła plums purchased from a Polish fruit processing factory. The average sugar content (sum of glucose, fructose and saccharose after inversion) was 11.8 ± 0.65 g/100 g, determined using HPLC *(17)*. To prepare mashes for fermentation, the destoned plums were homogenized into pulp. Comminuted stones, 10% of the whole stone fraction by weight, were added to the plum pulp. The prepared mash was supplemented with saccharose (10% *w*/w) and with $(NH_4)_2HPO_4$ (0.2 g/kg fruit pulp) as a nitrogen source for the yeast. Fermentation was initiated using the yeast *S. bayanus* (0.3 g/kg of plum pulp). This dry wine yeast has alcohol tolerance up to 18% *v*/v and a wide fermentation temperature spectrum (10–35°C; Fermentis, Division of S.I. Lesaffre, France).

### Fermentation

Alcoholic fermentation was performed in 12 containers of volume 50 L, each with 35 kg of inoculated plum mash. The vessels were sealed with air-tight covers which allowed the release of carbon dioxide ($CO_2$). They were kept in a room at 18 ± 1°C for 10 days. The process was continued until no further changes were observed in the apparent extract.

### Distillation

Distillation was performed in two ways: a two-stage process and a single-stage process. In the two-stage process, a first distillation was performed from fermented plum mash (35 kg, ethanol content 11.8 ± 1.9% *v*/v) in a copper alembic pot still working according to the law of parallel-current flow (Fig. 1a). The set-up consisted of a pot in which the mash was heated, a lyne arm which transferred steam to the cooler, and cooler in which the alcohol–water vapours were cooled. The alembic still was equipped with a water-steam jacket. The water-steam jacket was flame heated using a butane burner. The heating was set to obtain an average distillation rate of ~15 mL/min. The ethanol content of the raw distillate was 22 ± 4% *v*/v. In the second stage, ~18.5 L of the raw distillate was transferred to a counter-current flow working copper alembic still, consisting of a 50 L pot, an 80 cm-long column with a diameter of 15 cm filled with copper chips, a dephlegmator and a cooler (Fig. 1b). The raw distillate was subjected to fractional distillation and separated into three parts: the head fraction (first




a) copper alembic working accordingly to the law of parallel-current flow

b) copper alembic with column working accordingly to the law of counter-current flow

**Figure 1**. Alembics used to carry out the experiments.

overhead fraction), heart (middle) fractions with different alcohol contents and the tail fraction. In each variant of process the head fractions were collected under analogous conditions in quantities of ~10% of the volume of alcohol 100% *v*/v present in the raw distillate used in the re-distillation. The distillation flow rate of the head fractions was 13–14 mL/min. To obtain heart fractions with different alcohol contents, i.e. 70 ± 1, 75 ± 1, 83 ± 1, 86 ± 1 and 90 ± 1% *v*/v, the reflux rate was regulated by varying the coolant flow rate in the dephlegmator. The distillation flow rate of the heart fractions was between 35 mL/min for the fraction with a final ethanol content of 70 ± 1% *v*/v and 22 mL/min for the heart fraction with a final ethanol content of 90 ± 1% *v*/v. Ethanol concentration was measured with an areometer (calibrated in % *v*/v of ethanol at 20°C), immersed in the receiver. If the distillate temperature varied from 20°C then a correction was applied, using Alcoholometric Tables *(18)*. The calculation on the base of the volume and strength of the heart fractions revealed that they contained from 86% of the absolute alcohol present in the raw distillate (for the heart fraction with an ethanol content of 70 ± 1% *v*/v) to 79% of the absolute alcohol present in the raw distillate (for the heart fraction with an ethanol content of 90 ± 1% *v*/v).

Once heart fractions with the desired concentrations of ethanol had been obtained, the tail fractions were collected until the alcohol in the distillates was exhausted (the temperature of alcohol–water vapour in the distillation pot reached 100°C). As the alcohol content in the tail fraction decreased, the rate of distillation spontaneously reduced to 12–14 mL/min. Immediately after distillation of the tail fraction, the re-distillation process was stopped and the alembic still was allowed to cool. The distillation residue was removed, and the still was washed and left to dry before the next distillation.

In the single-stage process, a fermented plum mash (35 kg, ethanol content 11.8 ± 1.8% *v*/v) was transferred directly to an alembic column still (Fig. 1b) and fractional distillation was performed. Similar fractions were collected as in the case of the second phase of two-stage distillation: a head fraction approximately equivalent to 10% of the volume of 100% *v*/v alcohol present in the fermented plum mash (with a distillation flow rate of 13–14 mL/min); and heart fractions with final alcohol contents of 70 ± 1, 75 ± 1, 83 ± 1, 86 ± 1 and 90 ± 1% *v*/v (with distillation flow rates between 24 mL/min, for the fraction with a final ethanol content of 70 ± 1% *v*/v, and 14 mL/min for the heart fraction with a final ethanol content of 90 ± 1% *v*/v). The volumes of these fractions ranged from 86% of absolute alcohol present in the raw distillate (for the heart fraction with an ethanol content of 70 ± 1% *v*/v) to 79% of absolute alcohol present in the raw distillate (for the heart fraction with an ethanol content of 90 ± 1% *v*/v). As in the case of two-stage distillation, after obtaining heart fractions with the desired concentrations of ethanol, the tail fractions were collected. The next stages of the procedure were the same as for two-stage distillation.

### Analytical methods

An areometer calibrated for percentage of alcohol by volume was used to determine the ethanol contents of the fractions obtained from both single- and two-stage distillation. Chromatographic analysis of the volatile compounds in the distillates was performed using a GC apparatus (Agilent 7890A, USA) with a mass spectrometer (Agilent MSD 5975C, USA), following the method described by Pielech-Przybylska et al. *(17)*. Hydrocyanic acid content in the distillates was determined spectrophotometrically using pyridine–pyrazolon reagents, also as described by Pielech-Przybylska et al. *(17)*.

Ethyl carbamate content was determined according to the official AOAC method with some modifications *(19)*. To prepare the samples, 20–50 mL of tested fractions was mixed with internal standard propyl carbamate (1 mg/mL, 50 μL). An Extrelut® column was used, wrapped in aluminium foil to eliminate the possibility of light-induced EC forming during extraction. After 15 min of equilibration, the column was washed with *n*-pentane (2 × 20 mL). The analytes were then extracted using dichloromethane (3 × 50 mL). The eluates were combined in a brown flask, to which was added 5 mL of ethyl acetate. Next, the sample was reduced to 2–3 mL in a rotary evaporator (28°C, 300 mbar). The solution was adjusted to 10 mL using ethyl acetate in a measuring flask and injected directly into a GC/MS system. Analysis was conducted using a GC apparatus (Agilent 7890A, USA) with a mass spectrometer (Agilent MSD 5975C, USA). A DB-Wax column 123–7032 (30 m × 0.32 mm; 0.50 μm film thickness; Agilent, Santa Clara, CA, USA) was used to separate the EC. The temperature of the injector and detector interface was maintained at 260°C. The GC oven was programmed as follows: initial temperature 50°C (25 min), raised to 250°C at a rate of 5°C/ min, then held at this temperature for 10 min. The injected volume was 2.0 μL (splitless). Helium was used as the carrier gas, with a flow rate of 1.0 mL/min. The acquisition mode was selected ion monitoring, with monitoring ions *m/z* 62, 74 and 89. The recovery of EC was 100.5 ± 9.5%. The limits of detection (LOD) and quantitation (LOQ) were 0.01 and 0.04 mg/L of EC, respectively. The concentration of EC in the tested fractions was determined based on the calibration curve (0–0.8 mg/L). Quantitative analysis was performed using Agilent MassHunter (USA) software.

### Sensory analysis

Sensory assessment of the plum distillates was performed using the Buxbaum model of positive ranking *(20)*, described in our previous work *(17)*. The heart samples were diluted before sensory analysis to 40% *v*/v.

### Statistical analysis

All samples were prepared and analysed in triplicate. Results obtained were expressed as average ± SD. Statistical analyses were performed using STATISTICA 10 software (Statsoft, USA). The results were evaluated using analysis of variance (ANOVA), followed by Tukey's *post-hoc* test to verify statistical differences with a significance level of 0.05.

## Results and discussion

Volatile compounds of fruit distillates may originate from raw materials, as well as being formed as by-products during alcoholic fermentation, distillation and maturation *(20)*. Together with compounds responsible for aroma, fruit distillates contain undesirable compounds, such as methanol, HCN and EC, which can have adverse effects on human health. Therefore, during the distillation process the alcohol is separated into three fractions: the head, which mainly contains low-boiling-point compounds; the second (middle) fraction called the heart, which is the main product; and the tail, in which tend to distil compounds highly soluble in water and/or with high molecular weight *(21)*. It is

important to emphasize that the boiling point of compounds is not the sole criterion for their separation during distillation. The separation of compounds is strongly influenced by their solubility in alcohol and water mixture as well as by the distillation equipment employed. For instance, if the alembic still was used, the higher alcohol (2-methyl-1-butanol, 3-methyl-1-butanol, 2-methyl-1-propanol) content was higher in the heads and hearts than in the tails, despite their having boiling points $>$ 100°C. In turn, the solubility of the methanol in water, owing to its capacity to form hydrogen bridges, ensures that it is present in all fractions (often in the greatest concentration in tails), regardless of its lower boiling point *(22,23)*.

The composition of the volatile components in the obtained fractions of the plum distillate varied greatly depending on the distillation strategy (two-stage or single-stage) used and was also closely linked to the separation points, i.e. the head from the heart fractions, and the heart from the tail fractions. The chemical compositions of the obtained fractions are presented in Tables 1–3.

According to the literature *(24)*, head compounds typically include aliphatic aldehydes and esters (ethyl acetate, isoamyl acetate, methyl acetate), because of their low boiling points and high solubility in ethanol.

Of the aldehydes in the head fractions, acetaldehyde occurred in the largest concentrations ($p < 0.05$), regardless of the distillation variant used (two-stage or single-stage). Acetaldehyde can give beverages a fruity character when present in low concentrations, but in higher concentrations it causes a pungent smell, producing poor-quality distillates *(25,26)*. Moreover, it is a substance considered 'possibly carcinogenic to humans' by the IARC (Group 2B) *(27)*. Interestingly, the concentrations of acetaldehyde in the head fractions obtained from two-stage distillation were approximately double those obtained following the single-stage process ($p < 0.05$). The head fractions also contained large quantities (compared with the tail fractions) of other aldehydes, such as isobutyraldehyde, isovaleraldehyde and hexanal, as well as of acetaldehyde diethyl acetal ($p < 0.05$). As in the case of acetaldehyde, the concentrations of other aldehydes, i.e. isobutyraldehyde, isovaleraldehyde and hexanal, were significantly higher in heads obtained following two-stage distillation than after single-stage distillation ($p < 0.05$). This can be explained by the fact that, when a second distillation is performed, part of the water in the wash has already been removed by the first distillation, which increases the concentrations of ethanol and volatile secondary compounds in the second distillate *(28)*.

Furfural showed a different distribution from that of the aliphatic aldehydes. The highest concentrations were measured in the tail fractions, especially in those obtained after two-stage distillation ($p < 0.05$; see Table 1a). Our results for the distribution

**Table 1a.** Volatile profiles of head and tail fractions obtained from fractionation of two-stage plum distillate

| Compound (mg/L alcohol 100% *v*/v) | Plum distillate – head and tail fractions | | | | | | |
|---|---|---|---|---|---|---|---|
| | Two-stage distillation | | | | | | |
| | Head | Tail-70 | Tail-75 | Tail-80 | Tail-83 | Tail-86 | Tail-90 |
| Ethanol (% *v*/v) | $90.25^{A} \pm 0.52$ | $30.15^{b} \pm 0.62$ | $32.56^{BC} \pm 1.19$ | $34.19^{abc} \pm 2.33$ | $33.80^{abc} \pm 1.55$ | $33.69^{abc} \pm 1.18$ | $38.78^{ade} \pm 2.25$ |
| *Aldehydes* | | | | | | | |
| Acetaldehyde | $2475^{B} \pm 620$ | $10.58^{a} \pm 0.60$ | $10.27^{a} \pm 0.49$ | $11.07^{a} \pm 0.84$ | $11.22^{a} \pm 0.25$ | $12.98^{a} \pm 0.32$ | $12.07^{a} \pm 0.45$ |
| Isobutyraldehyde | $17.12^{B} \pm 3.34$ | n.d. | $0.28^{ae} \pm 0.03$ | $0.23^{abc} \pm 0.06$ | $0.16^{bcd} \pm 0.05$ | $0.22^{abc} \pm 0.05$ | $0.19^{abcd} \pm 0.02$ |
| Isovaleraldehyde | $35.98^{B} \pm 2.22$ | $0.45^{BC} \pm 0.11$ | $0.75^{d} \pm 0.05$ | $0.33^{ab} \pm 0.18$ | $0.64^{cd} \pm 0.04$ | $0.14^{a} \pm 0.02$ | $0.16^{a} \pm 0.02$ |
| Hexanal | $62.27^{B} \pm 2.16$ | n.d. | $0.08^{b} \pm 0.01$ | $0.13^{abcd} \pm 0.02$ | $0.10^{ab} \pm 0.01$ | $0.12^{abc} \pm 0.02$ | $0.09^{ab} \pm 0.01$ |
| Furfural | $0.64^{B} \pm 0.07$ | $642.96^{a} \pm 29.72$ | $646.96^{a} \pm 31.96$ | $577.45^{a} \pm 22.96$ | $586.96^{a} \pm 23.96$ | $592.45^{a} \pm 18.96$ | $617.45^{a} \pm 32.96$ |
| Benzaldehyde | $0.02^{A} \pm 0.00$ | $0.29^{ab} \pm 0.02$ | $0.24^{abc} \pm 0.04$ | $0.28^{ab} \pm 0.02$ | $0.28^{ab} \pm 0.03$ | $0.22^{ac} \pm 0.05$ | $0.19^{c} \pm 0.01$ |
| Acetaldehyde diethyl acetal | $57.19^{A} \pm 3.98$ | $1.34^{ac} \pm 0.05$ | $1.39^{abc} \pm 0.09$ | $1.70^{abc} \pm 0.08$ | $2.36^{bd} \pm 0.25$ | $2.98^{de} \pm 0.32$ | $2.07^{abd} \pm 0.15$ |
| *Higher alcohols* | | | | | | | |
| 1-Propanol | $1294.4^{A} \pm 306.9$ | $879.6^{abc} \pm 99.9$ | $879.6^{abc} \pm 97.9$ | $782.8^{abd} \pm 64.2$ | $727.2^{ad} \pm 33.8$ | $1085.1^{e} \pm 110.8$ | $1325.5^{g} \pm 22.34$ |
| 2-Methyl- 1-propanol | $1159.5^{A} \pm 220.9$ | $422.5^{bf} \pm 36.9$ | $394.5^{b} \pm 46.9$ | $82.5^{ac} \pm 5.9$ | $71.6^{a} \pm 5.5$ | $128.1^{acd} \pm 16.9$ | $343.9^{b} \pm 26.4$ |
| 1-Butanol | $1.99^{A} \pm 0.24$ | $3.15^{ac} \pm 0.26$ | $2.51^{ab} \pm 0.14$ | $2.36^{ab} \pm 0.35$ | $2.26^{ab} \pm 0.65$ | $14.48^{f} \pm 0.43$ | $21.86^{g} \pm 0.26$ |
| 2-Methyl- 1-butanol | $241.7^{A} \pm 42.1$ | $298.6^{ab} \pm 32.7$ | $286.8^{ab} \pm 28.67$ | $232.4^{a} \pm 33.8$ | $283.3^{ab} \pm 27.2$ | $240.7^{a} \pm 20.2$ | $451.9^{c} \pm 23.2$ |
| 3-Methyl- 1-butanol | $1463.0^{A} \pm 115.9$ | $969.7^{c} \pm 114.1$ | $1123.0^{BC} \pm 125.1$ | $1169.7^{BC} \pm 74.1$ | $1119.^{bc} \pm 103.9$ | $1381.3^{b} \pm 106.7$ | $1375.8^{b} \pm 222.8$ |
| 1-Hexanol | $3.12^{A} \pm 0.35$ | $90.15^{a} \pm 7.25$ | $88.65^{a} \pm 10.25$ | $75.03^{a} \pm 8.20$ | $85.90^{a} \pm 5.03$ | $127.33^{c} \pm 10.67$ | $195.55^{de} \pm 12.26$ |
| Benzyl alcohol | n.d. | $2.35^{b} \pm 0.25$ | $3.45^{BC} \pm 0.15$ | $4.49^{cd} \pm 0.36$ | $5.50^{ad} \pm 0.34$ | $6.32^{a} \pm 0.45$ | $8.15^{e} \pm 0.75$ |
| 2-Phenylethanol | $32.12^{A} \pm 2.36$ | $63.35^{abcd} \pm 5.25$ | $58.45^{abd} \pm 4.15$ | $44.49^{d} \pm 3.36$ | $50.50^{ad} \pm 4.34$ | $76.32^{abc} \pm 6.45$ | $85.15^{bce} \pm 7.75$ |
| *Esters* | | | | | | | |
| Methyl acetate | $76.26^{A} \pm 9.98$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Ethyl acetate | $3225.50^{A} \pm 25.15$ | $38.64^{d} \pm 3.54$ | $42.93^{ad} \pm 3.40$ | $65.55^{b} \pm 7.13$ | $47.18^{acd} \pm 5.96$ | $45.64^{ad} \pm 6.54$ | $47.76^{acd} \pm 7.35$ |
| Isoamyl acetate | $75.27^{A} \pm 6.16$ | $0.14^{c} \pm 0.03$ | $0.25^{BC} \pm 0.03$ | $0.27^{BC} \pm 0.04$ | $0.34^{BC} \pm 0.03$ | $0.45^{ab} \pm 0.05$ | $0.47^{ab} \pm 0.04$ |
| Ethyl butanoate | $6.95^{A} \pm 0.35$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Ethyl caproate | $16.60^{A} \pm 1.46$ | n.d. | $0.11^{abc} \pm 0.03$ | $0.17^{a} \pm 0.02$ | $0.10^{abc} \pm 0.02$ | $0.15^{ab} \pm 0.05$ | $0.17^{a} \pm 0.04$ |
| Ethyl caprylate | $133.06^{A} \pm 25.46$ | $8.50^{c} \pm 0.66$ | $7.11^{de} \pm 0.33$ | $9.17^{c} \pm 0.62$ | $8.10^{cd} \pm 0.52$ | $6.15^{e} \pm 0.35$ | $8.17^{cd} \pm 0.44$ |
| Ethyl caprate | $133.06^{A} \pm 25.46$ | $8.50^{c} \pm 0.66$ | $7.11^{de} \pm 0.33$ | $9.17^{c} \pm 0.62$ | $8.10^{cd} \pm 0.52$ | $6.15^{e} \pm 0.35$ | $8.17^{cd} \pm 0.44$ |

n.d., Not detected. Means in rows with different superscript capital letters are significantly different ($p < 0.05$) as analysed by one-way ANOVA. Means in rows with different superscript lowercase letters are significantly different ($p < 0.05$) as analysed by two-way ANOVA and the Tukey's *post-hoc* test.

of furfural following distillation are in agreement with those reported in the literature *(21,28)*.

Separating most of the aliphatic aldehydes in the head fractions resulted in reduced concentrations of these compounds in the heart fractions, i.e. final plum distillates ($p < 0.05$). However, as alcohol content in the heart fractions increased, a gradual decrease in the concentration of acetaldehyde was observed, in both the two-stage and the single-stage process ($p < 0.05$; see Table 2). Satora et al. *(29)* report the content of this compound in plum distillates as ranging from 123 mg/L (Stanley variety) to 298 mg/L of 100% *v*/v alcohol (Węgierka Dąbrowicka variety). The higher concentrations of acetaldehyde reported by the authors *(29)* are a consequence of the lower alcohol contents in the fractions they tested (from 67.4 ± 0.8 to 74.2 ± 1.3% *v*/v) and the use of a different distillation apparatus. The statistically significant ($p < 0.05$) differences between acetaldehyde contents in analogous heart fractions obtained following two-stage or single-stage processes were due to differences in the amounts of acetaldehyde in the separated head fractions. Single-stage distillation resulted in the separation of head fractions with acetaldehyde concentrations ~50% lower than those in head fractions separated following two-stage distillation ($p < 0.05$). Alcarde et al. *(28)* also observed that the chemical quality of spirits produced by double distillation was higher than that of spirits made using simple distillation, since double distillation resulted in an increase their purification degree. In our study, the concentrations of propionaldehyde, isobutyraldehyde, 2-methyl-butyraldehyde, isovaleraldehyde, hexanal, furfural and benzaldehyde were also correlated with the alcohol by volume strength of the heart fractions. The highest concentrations of these compounds were detected in hearts with ethanol contents of ~70 and 75% *v*/v. Their concentrations decreased as the alcohol content increased ($p < 0.05$).

The heart fractions obtained after double distillation were also characterized by significantly higher ($p < 0.05$) concentrations of furfural in comparison with corresponding hearts following single-stage distillation. Varying concentrations of furfural in spirit beverages can result from different distillation conditions and equipment *(30)*. Furfural is generated by the dehydration of pentoses *(31)*, and occurs during distillation involving Maillard reactions *(32)*. Its constant increase was probably due to furfural synthesis occurring in the heated pot still.

The flavour of stone fruit spirits is affected by the aroma compound benzaldehyde, which originates from the enzymatic degradation of amygdalin present in the stones of fruits *(33)*. Our results showed the highest concentrations of benzaldehyde in the heart fractions ($p < 0.05$; see Table 2a), which should be considered beneficial in terms of the sensory quality of the plum

**Table 1b.** Volatile profiles of head and tail fractions obtained from fractionation of single-stage plum distillate

| Compound (mg/L alcohol 100% *v*/v) | Plum distillate – head and tail fractions | | | | | | |
|---|---|---|---|---|---|---|---|
| | Single-stage distillation | | | | | | |
| | Head | Tail-70 | Tail- 75 | Tail-80 | Tail-83 | Tail-86 | Tail-90 |
| Ethanol (% *v*/v) | $88.87^{A} \pm 1.63$ | $36.47^{ace} \pm 0.77$ | $38.29^{ade} \pm 0.68$ | $42.00^{df} \pm 2.64$ | $40.32^{def} \pm 2.17$ | $43.20^{df} \pm 2.36$ | $44.75^{f} \pm 2.72$ |
| *Aldehydes* | | | | | | | |
| Acetaldehyde | $1165^{A} \pm 320$ | $49.87^{d} \pm 4.89$ | $62.76^{e} \pm 8.28$ | $77.36^{b} \pm 6.17$ | $88.18^{BC} \pm 5.12$ | $93.24^{c} \pm 3.98$ | $131.25^{f} \pm 2.45$ |
| Isobutyraldehyde | $5.18^{A} \pm 0.14$ | $0.45^{g} \pm 0.06$ | $0.39^{eg} \pm 0.04$ | $0.28^{ae} \pm 0.03$ | $0.26^{ac} \pm 0.03$ | $0.12^{bd} \pm 0.02$ | $0.09^{d} \pm 0.02$ |
| Isovaleraldehyde | $24.65^{A} \pm 3.14$ | $0.15^{a} \pm 0.02$ | $0.21^{a} \pm 0.03$ | $0.23^{a} \pm 0.02$ | $0.24^{a} \pm 0.04$ | $0.17^{a} \pm 0.02$ | $0.19^{a} \pm 0.02$ |
| Hexanal | $49.39^{A} \pm 5.36$ | $0.14^{acd} \pm 0.02$ | $0.13^{abcd} \pm 0.02$ | $0.16^{cd} \pm 0.02$ | $0.12^{abc} \pm 0.02$ | $0.14^{acd} \pm 0.02$ | $0.18^{d} \pm 0.03$ |
| Furfural | $0.34^{A} \pm 0.04$ | $225.96^{cd} \pm 18.36$ | $210.96^{d} \pm 15.36$ | $286.96^{BC} \pm 23.96$ | $292.45^{BC} \pm 18.96$ | $317.45^{b} \pm 32.96$ | $320.34^{b} \pm 22.04$ |
| Benzaldehyde | $0.03^{A} \pm 0.02$ | $0.19^{c} \pm 0.02$ | $0.25^{abc} \pm 0.04$ | $0.32^{b} \pm 0.02$ | $0.28^{ab} \pm 0.03$ | $0.25^{abc} \pm 0.04$ | $0.29^{ab} \pm 0.02$ |
| Acetaldehyde diethyl acetal | $89.75^{B} \pm 5.64$ | $5.56^{f} \pm 0.55$ | $7.70^{g} \pm 0.84$ | $3.36^{e} \pm 0.25$ | $1.98^{ab} \pm 0.22$ | $1.94^{abc} \pm 0.18$ | $0.97^{c} \pm 0.07$ |
| *Higher alcohols* | | | | | | | |
| 1-Propanol | $1341.6^{A} \pm 389.7$ | $400.1^{f} \pm 16.9$ | $332.6^{f} \pm 19.2$ | $685.4^{d} \pm 23.2$ | $860.5^{abcd} \pm 51.3$ | $947.1^{bce} \pm 60.8$ | $980.7^{ce} \pm 62.7$ |
| 2-Methyl- 1-propanol | $1289.6^{A} \pm 232.7$ | $68.8^{a} \pm 4.4$ | $177.6^{cde} \pm 26.4$ | $192.5^{de} \pm 21.9$ | $204.9^{e} \pm 23.2$ | $328.1^{b} \pm 22.5$ | $507.9^{f} \pm 48.4$ |
| 1-Butanol | $2.77^{A} \pm 0.54$ | $1.55^{b} \pm 0.17$ | $2.74^{a} \pm 0.34$ | $3.08^{ac} \pm 0.37$ | $4.00^{c} \pm 0.35$ | $5.32^{d} \pm 0.23$ | $7.99^{e} \pm 0.56$ |
| 2-Methyl- 1-butanol | $221.6^{A} \pm 42.2$ | $248.8^{a} \pm 35.7$ | $285.8^{ab} \pm 28.7$ | $232.9^{a} \pm 20.8$ | $333.8^{bd} \pm 15.2$ | $380.7^{cd} \pm 14.4$ | $451.9^{c} \pm 27.2$ |
| 3-Methyl- 1-butanol | $1220.0^{A} \pm 145.7$ | $161.7^{a} \pm 7.3$ | $157.9^{a} \pm 5.6$ | $181.7^{a} \pm 9.1$ | $132.2^{a} \pm 14.9$ | $281.3^{a} \pm 33.7$ | $265.8^{a} \pm 32.8$ |
| 1-Hexanol | $5.69^{B} \pm 0.35$ | $70.36^{a} \pm 9.14$ | $76.04^{a} \pm 2.14$ | $95.03^{ab} \pm 7.20$ | $121.90^{BC} \pm 15.03$ | $178.33^{d} \pm 15.67$ | $219.82^{e} \pm 13.76$ |
| Benzyl alcohol | $0.42^{B} \pm 0.03$ | $3.42^{BC} \pm 0.35$ | $5.68^{ad} \pm 0.47$ | $6.80^{ae} \pm 0.56$ | $6.87^{ae} \pm 0.53$ | $12.66^{f} \pm 0.24$ | $22.12^{g} \pm 1.36$ |
| 2-Phenylethanol | $59.42^{B} \pm 5.03$ | $90.42^{ce} \pm 7.35$ | $75.68^{abc} \pm 6.47$ | $108.80^{e} \pm 7.56$ | $163.87^{f} \pm 12.53$ | $182.66^{f} \pm 14.24$ | $229.12^{g} \pm 19.36$ |
| *Esters* | | | | | | | |
| Methyl acetate | $105.25^{B} \pm 12.45$ | n.d. | n.d. | n.d. | n.d. | n.d. | n.d. |
| Ethyl acetate | $5212.55^{B} \pm 355.60$ | $55.56^{abc} \pm 1.20$ | $58.56^{abc} \pm 4.22$ | $65.06^{b} \pm 6.42$ | $66.43^{b} \pm 5.25$ | $62.31^{BC} \pm 5.32$ | $58.33^{abc} \pm 7.12$ |
| Isoamyl acetate | $213.39^{B} \pm 14.36$ | $0.58^{a} \pm 0.13$ | $0.46^{ab} \pm 0.05$ | $0.57^{a} \pm 0.08$ | $0.66^{a} \pm 0.12$ | $0.59^{a} \pm 0.13$ | $0.62^{a} \pm 0.06$ |
| Ethyl butanoate | $10.24^{B} \pm 0.53$ | $0.11^{b} \pm 0.02$ | $0.14^{b} \pm 0.02$ | $0.12^{b} \pm 0.02$ | $0.14^{b} \pm 0.02$ | $0.12^{b} \pm 0.02$ | $0.19^{c} \pm 0.02$ |
| Ethyl caproate | $25.62^{B} \pm 1.55$ | n.d. | $0.055^{cd} \pm 0.002$ | $0.11^{abc} \pm 0.02$ | $0.13^{ab} \pm 0.02$ | $0.09^{BC} \pm 0.01$ | $0.12^{abc} \pm 0.02$ |
| Ethyl caprylate | $288.56^{B} \pm 25.46$ | $4.45^{b} \pm 0.66$ | $3.11^{a} \pm 0.15$ | $3.17^{ab} \pm 0.22$ | $3.10^{a} \pm 0.32$ | $3.15^{ab} \pm 0.35$ | $3.69^{ab} \pm 0.44$ |
| Ethyl caprate | $288.56^{B} \pm 25.46$ | $4.45^{b} \pm 0.66$ | $3.11^{a} \pm 0.15$ | $3.17^{ab} \pm 0.22$ | $3.10^{a} \pm 0.32$ | $3.15^{ab} \pm 0.35$ | $3.69^{ab} \pm 0.44$ |

**Table 2a.** Concentrations of aldehydes, acetals and higher alcohols in heart fractions from two-stage distillation

| Compound (mg/L alcohol 100% *v*/v) | Two-stage distillation | | | | | |
|---|---|---|---|---|---|---|
| | Heart-70 | Heart-75 | Heart-80 | Heart-83 | Heart-86 | Heart-90 |
| *Aldehydes and acetals* | | | | | | |
| Acetaldehyde | $51.14^{a} \pm 5.98$ | $45.39^{a} \pm 5.49$ | $39.70^{a} \pm 4.84$ | $43.36^{a} \pm 3.25$ | $42.98^{a} \pm 7.32$ | $39.07^{a} \pm 5.45$ |
| Propionaldehyde | $0.151^{g} \pm 0.002$ | $0.093^{f} \pm 0.004$ | $0.055^{b} \pm 0.003$ | $0.046^{ac} \pm 0.003$ | $0.064^{e} \pm 0.005$ | $0.051^{abc} \pm 0.003$ |
| Isobutyraldehyde | $1.86^{e} \pm 0.34$ | $1.89^{e} \pm 0.28$ | $0.98^{cd} \pm 0.07$ | $0.56^{a} \pm 0.05$ | $0.32^{ab} \pm 0.05$ | $0.19^{ab} \pm 0.02$ |
| 2-Methylbutyraldehyde | $0.55^{c} \pm 0.08$ | $0.49^{c} \pm 0.06$ | $0.25^{ab} \pm 0.05$ | $0.22^{ab} \pm 0.03$ | $0.16^{a} \pm 0.02$ | $0.15^{a} \pm 0.02$ |
| Isovaleraldehyde | $5.08^{c} \pm 0.22$ | $5.75^{cd} \pm 0.15$ | $4.13^{g} \pm 0.18$ | $3.64^{bg} \pm 0.24$ | $3.14^{ab} \pm 0.26$ | $1.16^{e} \pm 0.22$ |
| Hexanal | $3.39^{de} \pm 0.36$ | $3.14^{d} \pm 0.23$ | $4.00^{e} \pm 0.28$ | $3.53^{de} \pm 0.24$ | $2.15^{Bc} \pm 0.34$ | $1.22^{a} \pm 0.12$ |
| Furfural | $5.64^{f} \pm 0.77$ | $6.06^{f} \pm 0.96$ | $3.77^{b} \pm 0.26$ | $2.42^{ad} \pm 0.24$ | $2.93^{abd} \pm 0.21$ | $0.52^{c} \pm 0.06$ |
| Benzaldehyde | $2.86^{abc} \pm 0.34$ | $2.89^{abc} \pm 0.24$ | $2.18^{abd} \pm 0.22$ | $1.98^{ad} \pm 0.13$ | $1.82^{df} \pm 0.15$ | $0.89^{ef} \pm 0.07$ |
| Cinnamic aldehyde | $0.25^{c} \pm 0.02$ | $0.19^{ad} \pm 0.02$ | $0.15^{a} \pm 0.02$ | $0.14^{a} \pm 0.02$ | $0.06^{b} \pm 0.01$ | $0.05^{b} \pm 0.01$ |
| Acetaldehyde diethyl acetal | $32.94^{e} \pm 3.98$ | $35.39^{ef} \pm 3.49$ | $19.70^{d} \pm 1.84$ | $13.36^{cd} \pm 1.25$ | $12.98^{cd} \pm 1.32$ | $3.07^{ab} \pm 0.45$ |
| Hexanal diethyl acetal | $0.097^{e} \pm 0.010$ | $0.095^{e} \pm 0.008$ | $0.078^{be} \pm 0.008$ | $0.058^{ad} \pm 0.007$ | $0.060^{abd} \pm 0.004$ | $0.005^{c} \pm 0.001$ |
| *Higher alcohols* | | | | | | |
| 1-Propanol | $959.97^{f} \pm 126.91$ | $732.37^{e} \pm 99.99$ | $682.26^{e} \pm 53.21$ | $560.50^{de} \pm 44.53$ | $385.07^{bcd} \pm 30.84$ | $258.68^{abc} \pm 26.72$ |
| 2-Methyl- 1-propanol | $559.64^{g} \pm 22.96$ | $456.73^{f} \pm 56.92$ | $382.46^{bf} \pm 41.90$ | $364.99^{b} \pm 33.49$ | $328.10^{be} \pm 16.92$ | $243.94^{cde} \pm 24.37$ |
| 1-Butanol | $16.82^{h} \pm 1.24$ | $12.51^{g} \pm 1.14$ | $8.48^{f} \pm 0.97$ | $7.00^{ef} \pm 0.65$ | $4.48^{ad} \pm 0.43$ | $2.86^{abc} \pm 0.26$ |
| 2-Methyl- 1-butanol | $541.69^{f} \pm 42.12$ | $405.47^{ab} \pm 38.68$ | $358.96^{ab} \pm 33.77$ | $263.32^{d} \pm 27.15$ | $260.67^{d} \pm 24.38$ | $178.13^{c} \pm 13.17$ |
| 3-Methyl- 1-butanol | $1985.02^{g} \pm 135.95$ | $1777.80^{fg} \pm 125.10$ | $1181.68^{d} \pm 74.11$ | $919.19^{b} \pm 53.88$ | $681.32^{ab} \pm 36.66$ | $575.78^{ac} \pm 22.80$ |
| 1-Hexanol | $130.12^{f} \pm 10.35$ | $96.04^{e} \pm 8.14$ | $75.03^{d} \pm 8.20$ | $41.90^{c} \pm 3.03$ | $27.33^{a} \pm 1.67$ | $19.55^{ab} \pm 1.26$ |
| Benzyl alcohol | $0.088^{a} \pm 0.025$ | $0.063^{a} \pm 0.015$ | $0.058^{a} \pm 0.006$ | $0.029^{a} \pm 0.004$ | n.d. | n.d. |
| 2-Phenylethanol | $83.95^{b} \pm 6.25$ | $71.46^{bf} \pm 5.44$ | $53.75^{de} \pm 4.28$ | $33.72^{c} \pm 2.74$ | $17.95^{a} \pm 2.25$ | $5.68^{a} \pm 0.44$ |

n.d., Not detected. Means in rows with different superscript lowercase letters are significantly different ($p < 0.05$) as analysed by two-way ANOVA and the Tukey's *post-hoc* test.

distillate. The ethanol content in the heart fractions as well as distillation process strongly affected benzaldehyde concentration ($p < 0.05$). Higher ethanol concentrations in the heart fractions caused the concentration of benzaldehyde to decrease. Single-stage distillation produced higher concentrations of benzaldehyde than in the two-stage process.

Relatively small amounts of cinnamic aldehyde and acetals were detected in heart fractions. Their concentration was correlated only with the strength of heart fractions ($p < 0.05$), while no significant effect ($p > 0.05$) of distillation method was observed. Acetaldehyde diethyl acetal was separated in the head fractions at high concentrations ($p < 0.05$; see Table 1a, b), while hexanal diethyl acetal was only detected in the heart fractions, suggesting it had been formed during distillation.

Higher alcohols, also known as fusel alcohols, are the most important volatile compounds in fruit spirits from a quantitative point of view *(34–36)*. Higher alcohols are reported to contribute more to odour intensity than to the quality of wine *(30)*. The 'vegetal' and 'herbaceous' nuances given to wine by alcohols with six carbon atoms may constitute a defect depending on their concentrations *(37)*.

Despite the relatively high boiling temperatures of higher alcohols, they were present in relatively high concentrations in head fractions obtained following fractional distillation of plum spirits (Table 1a, b). This is probably due to their low solubility in water *(24)*. Higher alcohols were present in lower amounts in the heart and tail fractions, and a relationship was observed between the strength of alcohol by volume in the heart fractions (which determined their separation points from the tail fractions) and the higher alcohol contents in those fractions ($p < 0.05$). Satora et al. *(29)* report similar results during distillation of plum spirits from different varieties of plum.

The tail fractions obtained during two-stage distillation contained several times higher concentrations of 3-methyl-1-butanol than analogous samples after the single-stage process. This was again probably connected to the fact that during two-stage distillation part of the water in the wash has already been removed by the first distillation, raising the concentration of ethanol and volatile compounds in the second distillate *(28)*.

On the other hand, the quantities of 1-butanol were lowest in the head fractions ($p < 0.05$) and the higher ethanol concentrations in the middle fractions (from 70 to 90% *v*/v) resulted in a gradual increase in the concentration of 1-butanol in the tails. The highest ($p < 0.05$) concentrations of 1-hexanol, benzyl alcohol and 2-phenylethanol occurred mainly in the tail fractions, especially in the cases of 1-hexanol and benzyl alcohol. The concentrations in these fractions showed a pronounced tendency to increase as the alcohol content increased (from 70 to 90% *v*/v) in the middle fractions. Moreover, it was observed that the tails obtained after two-stage distillation contained lower ($p < 0.05$) concentrations of 1-hexanol, benzyl alcohol and 2-phenylethanol than the corresponding fractions obtained after single-stage distillation. This may be a consequence of a portion of these compounds being removed with the distillation residue from the first distillation.

With regards to fusel alcohols in heart fractions, their highest concentrations were observed in hearts with alcohol contents of 70% *v*/v and displayed a downwards tendency as the alcohol concentration increased ($p < 0.05$). The corresponding tail

**Table 2b.** Concentrations of aldehydes, acetals and higher alcohols in heart fractions from single-stage distillation

| Compound (mg/L alcohol 100% *v*/v) | Single-stage distillation | | | | | |
|---|---|---|---|---|---|---|
| | Heart-70 | Heart-75 | Heart-80 | Heart-83 | Heart-86 | Heart-90 |
| *Aldehydes and acetals* | | | | | | |
| Acetaldehyde | $135.25^{d} \pm 7.45$ | $110.46^{b} \pm 8.28$ | $99.36^{b} \pm 6.17$ | $78.18^{c} \pm 5.12$ | $53.24^{a} \pm 3.98$ | $49.15^{a} \pm 2.45$ |
| Propionaldehyde | $0.054^{BC} \pm 0.002$ | $0.056^{be} \pm 0.003$ | $0.044^{a} \pm 0.003$ | $0.043^{a} \pm 0.002$ | $0.031^{d} \pm 0.002$ | $0.033^{d} \pm 0.001$ |
| Isobutyraldehyde | $1.18^{d} \pm 0.14$ | $0.99^{cd} \pm 0.08$ | $0.58^{ac} \pm 0.06$ | $0.36^{ab} \pm 0.05$ | $0.12^{a} \pm 0.02$ | $0.19^{ab} \pm 0.02$ |
| 2-Methylbutyraldehyde | $0.45^{ce} \pm 0.06$ | $0.33^{be} \pm 0.05$ | $0.30^{b} \pm 0.04$ | $0.24^{ab} \pm 0.05$ | $0.12^{ad} \pm 0.02$ | n.d. |
| Isovaleraldehyde | $6.12^{d} \pm 0.42$ | $5.55^{cd} \pm 0.45$ | $3.13^{ab} \pm 0.28$ | $2.84^{af} \pm 0.24$ | $2.14^{f} \pm 0.23$ | $0.76^{e} \pm 0.15$ |
| Hexanal | $2.27^{c} \pm 0.16$ | $2.14^{BC} \pm 0.23$ | $2.00^{BC} \pm 0.28$ | $1.53^{ab} \pm 0.14$ | $1.15^{a} \pm 0.14$ | $1.22^{a} \pm 0.12$ |
| Furfural | $3.54^{bd} \pm 0.37$ | $4.06^{b} \pm 0.36$ | $2.17^{a} \pm 0.26$ | $2.12^{ae} \pm 0.21$ | $0.93^{ce} \pm 0.21$ | $0.12^{c} \pm 0.02$ |
| Benzaldehyde | $4.33^{g} \pm 0.38$ | $4.89^{g} \pm 0.62$ | $3.18^{c} \pm 0.42$ | $2.98^{BC} \pm 0.33$ | $2.82^{abc} \pm 0.35$ | $0.66^{e} \pm 0.08$ |
| Cinnamic aldehyde | $0.24d^{cd} \pm 0.03$ | $0.25^{c} \pm 0.03$ | $0.14^{a} \pm 0.02$ | $0.17^{a} \pm 0.02$ | $0.03^{b} \pm 0.02$ | $0.03^{b} \pm 0.01$ |
| Acetaldehyde diethyl acetal | $41.94^{f} \pm 5.98$ | $29.56^{e} \pm 1.55$ | $9.70^{BC} \pm 0.84$ | $5.36^{ab} \pm 0.25$ | $2.98^{ab} \pm 0.32$ | $0.17^{a} \pm 0.03$ |
| Hexanal diethyl acetal | $0.065^{ab} \pm 0.008$ | $0.072^{ab} \pm 0.011$ | $0.044^{df} \pm 0.005$ | $0.034^{f} \pm 0.006$ | $0.005^{c} \pm 0.002$ | n.d. |
| *Higher alcohols* | | | | | | |
| 1-Propanol | $529.93^{de} \pm 116.92$ | $432.37^{cd} \pm 99.19$ | $282.26^{abc} \pm 33.21$ | $260.50^{abc} \pm 21.33$ | $185.07^{ab} \pm 20.84$ | $98.68^{a} \pm 6.72$ |
| 2-Methyl- 1-propanol | $389.64^{bf} \pm 32.66$ | $256.63^{de} \pm 36.42$ | $182.46^{acd} \pm 21.90$ | $164.99^{ac} \pm 13.16$ | $128.10^{a} \pm 16.52$ | $93.94^{a} \pm 8.37$ |
| 1-Butanol | $6.77^{ef} \pm 0.54$ | $6.11^{de} \pm 0.34$ | $4.48^{ad} \pm 0.37$ | $3.00^{ac} \pm 0.35$ | $1.98^{BC} \pm 0.23$ | $0.99^{b} \pm 0.06$ |
| 2-Methyl- 1-butanol | $421.64^{b} \pm 32.12$ | $385.67^{ab} \pm 28.68$ | $330.96^{ad} \pm 23.77$ | $163.82^{c} \pm 17.15$ | $100.67^{ce} \pm 14.38$ | $78.99^{e} \pm 7.17$ |
| 3-Methyl- 1-butanol | $1567.02^{ef} \pm 125.65$ | $1377.80^{de} \pm 115.62$ | $881.68^{b} \pm 79.11$ | $732.19^{ab} \pm 64.88$ | $481.32^{ac} \pm 46.66$ | $385.78^{c} \pm 32.80$ |
| 1-Hexanol | $28.69^{ac} \pm 2.35$ | $26.04^{a} \pm 2.14$ | $25.03^{a} \pm 2.20$ | $21.90^{ab} \pm 1.03$ | $27.33^{a} \pm 1.64$ | $9.82^{b} \pm 0.76$ |
| Benzyl alcohol | $2.42^{e} \pm 0.17$ | $1.46^{d} \pm 0.15$ | $0.68^{c} \pm 0.06$ | $0.47^{b} \pm 0.03$ | n.d. | n.d. |
| 2-Phenylethanol | $97.75^{g} \pm 8.52$ | $81.95^{b} \pm 6.25$ | $63.69^{ef} \pm 4.39$ | $44.65^{cd} \pm 4.25$ | $13.95^{a} \pm 3.12$ | $6.25^{a} \pm 0.45$ |

fractions showed the opposite tendency. The following higher alcohols were present in the heart fractions (in descending order): 3-methyl-1-butanol, 1-propanol, 2-methyl-1-propanol, 2-methyl-1-butanol, 1-hexanol and 1-butanol. The concentrations of 1-butanol in the middle fractions were higher than those in the head and tail fractions. The heart fractions obtained after double-stage distillation contained significantly higher concentrations of fusel alcohols than the analogous fractions from single-stage distillation ($p < 0.05$). An inverse relationship was observed between the distillation technique and the concentration of benzyl alcohol. Benzyl alcohol was detected in much higher quantities in heart fractions (70–83% *v*/v) produced from single-stage distillation than those obtained in the double-stage process.

As mentioned above, compounds that are soluble in water and/or have high molecular weights tended to distil in the tail fractions *(21)*. This was the case with 2-phenylethanol, which gives a pleasant aroma to distillates *(38)*. In our study, an effect of ethanol content in heart fractions on the concentration of 2-phenylethanol was observed ($p < 0.05$) and its highest concentrations were revealed in heart fractions with 70% *v*/v alcohol content, whereas the lowest concentrations of this compound were in fractions containing 90% *v*/v alcohol ($p < 0.05$; see Table 2a, b). The corresponding tail fractions showed the opposite tendency (see Table 1a, b).

Esters contribute to the pleasant fruity aroma of fruit distillates *(20,33)*. The main ester produced by yeast during fermentation is ethyl acetate. At low concentrations (up to 200 mg/L) ethyl acetate has a floral and fruity aroma *(39)*. At higher concentrations it has a negative effect on the sensory quality of spirits, and its presence is related to acetic bacterial spoilage *(30)*. Esters are also the major volatile components in fresh plums *(40)*. According to the literature *(41,42)*, esters of acetic acid and alcohols such as propyl acetate, butyl acetate and hexyl acetate occur in fresh plums. Acetate esters of higher alcohols are significant aroma compounds in alcoholic beverages. These compounds can give a pleasant fruity fragrance to the general aroma of fruit distillates *(20)*. Esters have limited solubility in water, so they are distilled in the first moments of the process by steam stripping *(21)*. The higher concentrations of esters with high boiling points in the head fractions may be explained by the fact they form azeotropes with water and/or ethanol, which have boiling points lower than those of the individual components.

As shown in Table 1a, b, in our study esters were separated mainly in the head fractions. As a consequence, the concentrations of these compounds were much lower in the heart fractions (see Table 3a, b). Of the esters in the heart fractions, ethyl acetate was present in the highest concentrations, regardless of the distillation method used (two-stage or single-stage) ($p > 0.05$). Our results did not show a clear relationship between the distillation method and ethanol content on ethyl acetate concentrations in heart fractions ($p > 0.05$). Other esters, such as isobutyl acetate, 2-methyl-butyl acetate, amyl acetate, isoamyl acetate, hexyl acetate, 2-phenylethyl acetate and ethyl butanoate were present in relatively low concentrations. According to Williams and Ismail *(43)*, ethyl butanoate also plays an important part in the creation of aroma in European plums. The concentrations of acetate esters of higher alcohols and ethyl butanoate were higher in the majority of heart fractions obtained following double-stage distillation than in analogous samples derived during the single-stage process ($p < 0.05$).

The heart fractions of the plum distillates also contained esters of fatty acids C6–C10, i.e. ethyl caproate (hexanoate), ethyl caprylate (heptanoate), 2-phenylethyl caprylate, isoamyl caproate and ethyl caprate (decanoate). Most of these were also reported in plum distillates (67.4% *v*/v) by Satora et al. *(29)*. However, when analogous heart fractions from Wegierka Zwykła plums are

**Table 3a.** Concentrations of esters and terpenic compounds in heart fractions – two-stage distillation

| Compound (mg/L alcohol 100% *v*/v) | Two-stage distillation | | | | | |
|---|---|---|---|---|---|---|
| | Heart-70 | Heart-75 | Heart-80 | Heart-83 | Heart-86 | Heart-90 |
| *Esters* | | | | | | |
| Methyl acetate | $0.015^{BC} \pm 0.02$ | $0.009^{a} \pm 0.01$ | $0.011^{ab} \pm 0.02$ | $0.008^{a} \pm 0.01$ | $0.009^{a} \pm 0.01$ | $0.008^{a} \pm 0.01$ |
| Ethyl acetate | $428.50^{b} \pm 25.35$ | $444.69^{be} \pm 29.82$ | $397.20^{bd} \pm 25.04$ | $341.84^{cd} \pm 15.88$ | $335.82^{c} \pm 16.11$ | $147.25^{a} \pm 13.00$ |
| Isobutyl acetate | $0.055^{f} \pm 0.009$ | $0.075^{g} \pm 0.008$ | $0.025^{cde} \pm 0.002$ | $0.033^{de} \pm 0.006$ | $0.015^{ac} \pm 0.002$ | $0.005^{ab} \pm 0.002$ |
| 2-Methylbutyl acetate | $0.012^{ab} \pm 0.003$ | $0.015^{ab} \pm 0.002$ | $0.011^{ab} \pm 0.002$ | $0.013^{ab} \pm 0.004$ | $0.011^{ab} \pm 0.002$ | $0.008^{a} \pm 0.003$ |
| Amyl acetate | $0.312^{f} \pm 0.015$ | $0.415^{g} \pm 0.025$ | $0.111^{b} \pm 0.012$ | $0.213^{e} \pm 0.034$ | $0.051^{acd} \pm 0.014$ | $0.012^{a} \pm 0.003$ |
| Isoamyl acetate | $9.15^{e} \pm 0.98$ | $8.79^{e} \pm 0.75$ | $3.87^{cd} \pm 0.25$ | $4.34^{d} \pm 0.59$ | $3.37^{cd} \pm 0.47$ | $0.88^{a} \pm 0.10$ |
| Hexyl acetate | $0.038^{e} \pm 0.005$ | $0.034^{e} \pm 0.008$ | $0.018^{cd} \pm 0.003$ | $0.010^{abc} \pm 0.001$ | $0.006^{ab} \pm 0.002$ | n.d. |
| 2-Phenylethyl acetate | $0.165^{e} \pm 0.015$ | $0.115^{c} \pm 0.020$ | $0.111^{cd} \pm 0.014$ | $0.085^{acd} \pm 0.036$ | $0.051^{ab} \pm 0.009$ | $0.045^{ab} \pm 0.008$ |
| Ethyl butanoate | $0.36^{de} \pm 0.05$ | $0.33^{d} \pm 0.06$ | $0.19^{a} \pm 0.02$ | $0.34^{de} \pm 0.03$ | $0.18^{a} \pm 0.02$ | $0.07^{BC} \pm 0.01$ |
| Ethyl caproate | $3.88^{e} \pm 0.58$ | $2.70^{d} \pm 0.17$ | $1.85^{c} \pm 0.23$ | $1.92^{c} \pm 0.13$ | $0.95^{a} \pm 0.08$ | $0.80^{a} \pm 0.04$ |
| Ethyl caprylate | $56.65^{d} \pm 3.24$ | $49.52^{bd} \pm 2.35$ | $44.66^{b} \pm 5.72$ | $44.46^{b} \pm 6.47$ | $15.41^{a} \pm 1.22$ | $15.69^{a} \pm 1.16$ |
| 2-Phenylethyl caprylate | $0.005^{BC} \pm 0.002$ | $0.007^{c} \pm 0.002$ | $0.004^{abc} \pm 0.001$ | $0.002^{ab} \pm 0.001$ | $0.002^{ab} \pm 0.001$ | n.d. |
| Isoamyl caproate | $0.008^{a} \pm 0.002$ | $0.006^{ab} \pm 0.002$ | $0.005^{ab} \pm 0.001$ | $0.006^{ab} \pm 0.001$ | $0.003^{BC} \pm 0.001$ | n.d. |
| Ethyl caprate | $15.75^{f} \pm 1.30$ | $11.16^{de} \pm 2.16$ | $11.5^{de} \pm 2.67$ | $5.88^{BC} \pm 0.58$ | $3.70^{ab} \pm 0.27$ | $0.85^{a} \pm 0.13$ |
| Methyl benzoate | $0.008^{cd} \pm 0.002$ | $0.009^{d} \pm 0.002$ | $0.005^{bcd} \pm 0.001$ | $0.003^{ab} \pm 0.001$ | $0.003^{ab} \pm 0.001$ | n.d. |
| Ethyl benzoate | $12.35^{g} \pm 0.98$ | $9.05^{cd} \pm 0.85$ | $10.12^{d} \pm 0.44$ | $9.02^{cd} \pm 0.13$ | $7.25^{ab} \pm 0.55$ | $6.09^{a} \pm 0.22$ |
| Ethyl cinnamate | $0.065^{g} \pm 0.009$ | $0.039^{f} \pm 0.005$ | $0.025^{e} \pm 0.002$ | $0.013^{BC} \pm 0.001$ | $0.005^{ab} \pm 0.001$ | n.d. |
| *Terpenic compounds* | | | | | | |
| Linalyl acetate | $0.006^{b} \pm 0.003$ | $0.004^{ab} \pm 0.002$ | $0.004^{ab} \pm 0.001$ | $0.003^{ab} \pm 0.001$ | $0.001^{a} \pm 0.001$ | n.d. |
| Neryl acetate | $0.005^{BC} \pm 0.002$ | $0.007^{c} \pm 0.002$ | $0.004^{abc} \pm 0.001$ | $0.002^{ab} \pm 0.001$ | $0.002^{ab} \pm 0.001$ | n.d. |
| $\alpha$-Terpineol | $0.075^{abcd} \pm 0.015$ | $0.095^{acd} \pm 0.020$ | $0.105^{ad} \pm 0.014$ | $0.085^{acd} \pm 0.036$ | $0.031^{bef} \pm 0.005$ | $0.005^{a} \pm 0.002$ |

n.d., Not detected. Means in rows with different superscript lowercase letters are significantly different ($p < 0.05$) as analysed by two-way ANOVA and the Tukey's *post-hoc* test.

compared, the distillate obtained in our study (approximate alcohol content 70% *v*/v) contained much higher concentrations of fatty acids esters. This indicates that the quality of fruit distillates may vary depending on the distillation conditions and the type of equipment used.

Benzoates, salicylates *(44,45)* and cinnamates *(46)* make important contributions to the characteristic odours of plum brandy. Higher amounts of benzoates, especially ethyl benzoate, were detected in heart fractions obtained following double-stage distillation than in heart fractions obtained in the single-stage process ($p < 0.05$). Higher reflux and lower rates of distillation produced heart fractions with higher concentrations of ethanol and lower concentrations of aroma compounds. The heart fractions also contained low concentrations (<0.1 mg/L alcohol 100% *v*/v) of terpenic compounds and its derivatives, such as $\alpha$-terpineol, linalyl acetate and neryl acetate, probably originating from the raw material *(41)*.

## Compounds harmful to human health

**Methanol.** Methanol is subject to restrictions owing to its high toxicity *(9)*. Given the low boiling point of methanol (64.7°C) and its high volatility, it might be assumed that the highest concentrations of this compound would be present in the head fractions. Methanol should be distilled mainly at the beginning of the process, and its concentration may be expected to decrease steadily along the distillation path. According to the literature *(23,47,48)*, however, methanol concentrations show an unexpected increase towards the end of the distillation process. When distillation is performed with ethanol solutions <40% *v*/v, methanol also occurs in significant quantities in the tail fractions *(49)*. This is confirmed by the results presented in Fig. 2. The high concentrations of methanol in the tail fractions are probably due to the association phenomenon, as hydrogen bonds are created between water molecules and e.g. alcohols, which was confirmed by others authors *(22)*. As a consequence, an increase in the molecular weight and a decrease in the volatility of compounds (such as methanol) may be observed.

Methanol was present in all fractions obtained during distillation. The heart fractions contained different levels of this compound, depending on the alcohol by volume strength ($p < 0.05$). The lowest levels of methyl alcohol were in heart fractions with an alcohol content of 90% *v*/v, while the highest were in heart fractions with 70% alcohol by volume. As a consequence, in distillation variants in which the hearts contained the highest alcohol contents and the lowest levels of methanol, the tail fractions contained the highest concentrations of this undesirable compound ($p < 0.05$). The same relationship was observed for samples obtained during both two-stage and single-stage distillation. The heart fractions obtained after double distillation also contained higher ($p < 0.05$) concentrations of methanol than analogous fractions

**Table 3b.** Concentrations of esters and terpenic compounds in heart fractions – single stage distillation

| Compound (mg/L alcohol 100% *v*/v) | Single-stage distillation | | | | | |
|---|---|---|---|---|---|---|
| | Heart-70 | Heart-75 | Heart-80 | Heart-83 | Heart-86 | Heart-90 |
| *Esters* | | | | | | |
| Methyl acetate | $0.025^{d} \pm 0.02$ | $0.019^{c} \pm 0.02$ | $0.015^{BC} \pm 0.02$ | $0.018^{c} \pm 0.02$ | $0.012^{ab} \pm 0.01$ | $0.008^{a} \pm 0.01$ |
| Ethyl acetate | $507.55^{f} \pm 25.35$ | $490.33^{f} \pm 22.35$ | $132.91^{a} \pm 15.35$ | $115.89^{a} \pm 25.42$ | $138.69^{a} \pm 10.65$ | $113.42^{a} \pm 8.67$ |
| Isobutyl acetate | $0.024^{cd} \pm 0.002$ | $0.037^{e} \pm 0.005$ | $0.005^{ab} \pm 0.001$ | $0.005^{ab} \pm 0.001$ | $0.017^{ac} \pm 0.002$ | n.d. |
| 2-Methylbutyl acetate | $0.014^{ab} \pm 0.002$ | $0.017^{b} \pm 0.005$ | $0.015^{ab} \pm 0.002$ | $0.008^{a} \pm 0.001$ | $0.009^{a} \pm 0.002$ | n.d. |
| Amyl acetate | $0.214^{e} \pm 0.032$ | $0.117^{b} \pm 0.015$ | $0.095^{bd} \pm 0.022$ | $0.068^{bcd} \pm 0.015$ | $0.009^{a} \pm 0.002$ | $0.013^{ac} \pm 0.001$ |
| Isoamyl acetate | $3.32^{cd} \pm 1.23$ | $2.62^{BC} \pm 0.29$ | $1.14^{ab} \pm 0.15$ | $1.35^{ab} \pm 0.25$ | $1.00^{ab} \pm 0.08$ | $1.20^{ab} \pm 0.15$ |
| Hexyl acetate | $0.028^{de} \pm 0.007$ | $0.014^{BC} \pm 0.003$ | $0.018^{cd} \pm 0.002$ | $0.010^{abc} \pm 0.001$ | $0.004^{ab} \pm 0.001$ | n.d. |
| 2-Phenylethyl acetate | $0.114^{c} \pm 0.012$ | $0.118^{c} \pm 0.015$ | $0.065^{ad} \pm 0.012$ | $0.055^{ab} \pm 0.015$ | $0.039^{ab} \pm 0.002$ | $0.017^{b} \pm 0.003$ |
| Ethyl butanoate | $0.44^{ef} \pm 0.05$ | $0.50^{f} \pm 0.07$ | $0.12^{ab} \pm 0.02$ | $0.15^{ab} \pm 0.02$ | $0.09^{abc} \pm 0.01$ | n.d. |
| Ethyl caproate | $2.61^{d} \pm 0.15$ | $2.45^{cd} \pm 0.25$ | $0.85^{a} \pm 0.07$ | $0.35^{ab} \pm 0.05$ | $0.09^{b} \pm 0.02$ | n.d. |
| Ethyl caprylate | $22.69^{a} \pm 1.16$ | $22.19^{a} \pm 1.63$ | $14.66^{a} \pm 1.72$ | $14.46^{a} \pm 1.47$ | $3.41^{c} \pm 0.22$ | $1.69^{c} \pm 0.16$ |
| 2-Phenylethyl caprylate | $0.004^{abc} \pm 0.002$ | $0.005^{BC} \pm 0.002$ | $0.003^{abc} \pm 0.002$ | $0.002^{ab} \pm 0.001$ | $0.002^{ab} \pm 0.001$ | n.d. |
| Isoamyl caproate | $0.007^{ab} \pm 0.002$ | $0.008^{a} \pm 0.002$ | $0.005^{ab} \pm 0.002$ | $0.004^{abc} \pm 0.001$ | n.d. | n.d. |
| Ethyl caprate | $7.35^{c} \pm 1.13$ | $13.24^{ef} \pm 1.35$ | $9.32^{cd} \pm 0.75$ | $2.85^{ab} \pm 0.35$ | $0.65^{a} \pm 0.07$ | $0.15^{a} \pm 0.03$ |
| Methyl benzoate | $0.005^{bcd} \pm 0.002$ | $0.003^{ab} \pm 0.002$ | $0.003^{ab} \pm 0.002$ | $0.004^{abc} \pm 0.001$ | $0.003^{ab} \pm 0.001$ | n.d. |
| Ethyl benzoate | $7.75^{BC} \pm 0.63$ | $5.81^{a} \pm 0.32$ | $6.36^{ab} \pm 0.50$ | $3.45^{ef} \pm 0.28$ | $4.25^{f}$ 0.36 | $2.01^{e} \pm 0.12$ |
| Ethyl cinnamate | $0.035^{f} \pm 0.004$ | $0.023^{de} \pm 0.002$ | $0.015^{cd} \pm 0.002$ | $0.004^{ab} \pm 0.001$ | $0.005^{ab} \pm 0.001$ | n.d. |
| *Terpenic compounds* | | | | | | |
| Linalyl acetate | $0.004^{ab} \pm 0.002$ | $0.004^{ab} \pm 0.002$ | $0.003^{ab} \pm 0.002$ | $0.002^{ab} \pm 0.001$ | $0.002^{ab} \pm 0.001$ | n.d. |
| Neryl acetate | $0.004^{abc} \pm 0.002$ | $0.005^{BC} \pm 0.002$ | $0.003^{abc} \pm 0.002$ | $0.002^{ab} \pm 0.001$ | $0.002^{ab} \pm 0.001$ | n.d. |
| $\alpha$-Terpineol | $0.114^{a} \pm 0.012$ | $0.118^{a} \pm 0.015$ | $0.065^{bcd} \pm 0.012$ | $0.055^{bcf} \pm 0.015$ | $0.039^{bef} \pm 0.002$ | $0.017^{ef} \pm 0.003$ |

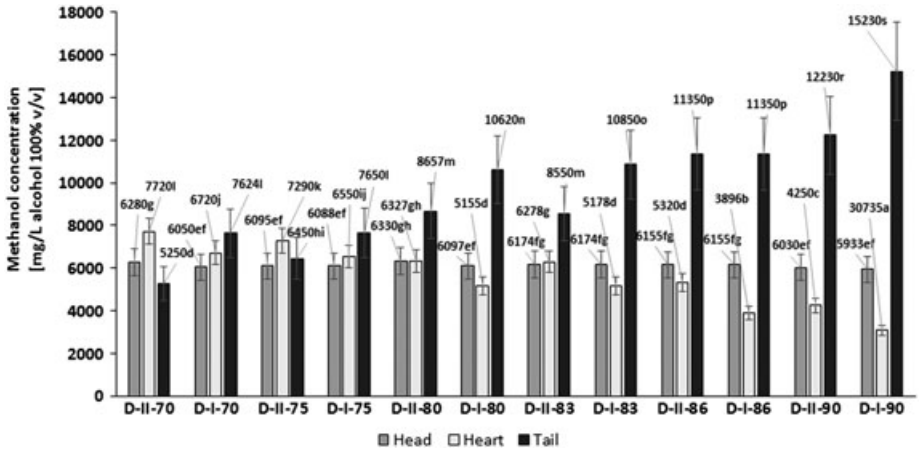



**Figure 2.** Methanol distribution in fractions obtained during distillation of plum spirit. Means with different letters are significantly different ($p < 0.05$) as analysed by three-way ANOVA and the Tukey's *post-hoc* test.

derived during the single-stage process. However, no conclusion can be drawn on the basis of these results regarding the quality of plum distillates obtained from single- or double-stage distillation in terms of methanol content, since all the heart fractions obtained fulfilled the requirements of EU Regulation (EC) no. 110/2008 *(8)*.

**Hydrocyanic acid and ethyl carbamate.** To effectively separate low-boiling compounds, including HCN with a boiling point of 25.6°C, it is important to separate the appropriate amounts of head fractions. Figure 3 shows the distribution of HCN in the fractions obtained in our study. The results of three-way ANOVA showed a significant effect of distillation method and kind of fraction, as well as of alcoholic strength of heart fractions on the distribution of HCN ($p < 0.05$). As can be seen, in the case both of double-stage and single-stage distillation, the highest concentrations of HCN were found in head fractions. Concentrations of this compound in the head fractions were

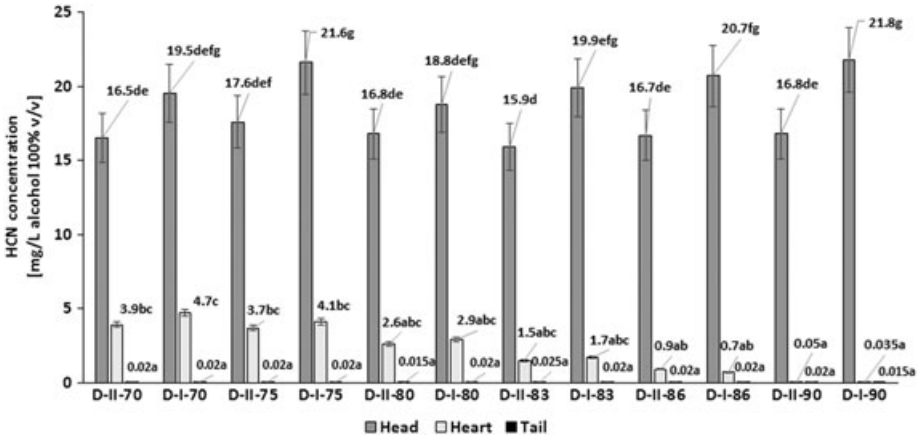



**Figure 3**. Hydrocyanic acid distribution in fractions obtained during distillation of plum spirit. Means with different letters are significantly different ($p < 0.05$) as analysed by three-way ANOVA and the Tukey's *post-hoc* test.

slightly higher following the single-stage process, at between 18.8 and 21.8 mg/L of 100% *v*/v alcohol ($p < 0.05$). The heart fractions had significantly lower HCN contents ($p < 0.05$). In hearts with 70% *v*/v alcohol content the concentration of HCN was between 3.9 mg/L of 100% *v*/v alcohol (for double-stage distillation) and 4.7 mg/L alcohol 100% *v*/v (for single-stage distillation; $p > 0.05$). Increasing the alcohol by volume strength of the heart fractions resulted in a gradual decrease in HCN concentrations ($p < 0.05$). In fractions with 90% *v*/v alcohol the HCN content was very low, at between 0.035 and 0.050 mg/L of 100% *v*/v alcohol. However, it should be emphasized that, irrespective of the distillation method used, the concentrations of this compound in all the tested heart fractions were within the limits specified by the EU Regulation for stone fruit distillates *(8)*. The tail fractions contained traces of HCN, at levels not exceeding 0.02 mg/L of 100% *v*/v alcohol.

Reducing the HCN content in fruit distillates is necessary not only because of its toxicity but also because HCN is one of the precursors of EC. Ethyl carbamate may contribute to the carcinogenicity of alcoholic beverages *(50)* owing to the synergistic effects between ethanol, EC and other possible carcinogenic contaminants in foods co-ingested with alcoholic beverages *(51)*.

All head fractions obtained from double-stage distillation as well as in the single-stage process contained EC in amounts close to the detection limit, while the highest concentrations of EC were detected in the tail fractions ($p < 0.05$) (see Fig. 4). Hesford and Schneider *(52)* suggest that EC synthesis is promoted by longer vapour residence times at high temperatures, but the results of our study did not show clearly the effect of distillation method on EC distribution ($p > 0.05$). Importantly, it should be emphasized that in all heart fractions the concentrations of EC were below the limit set by the European Commission for alcoholic beverages, at ≤1.0 mg/L *(53)*.

## Sensory evaluation

The differences in the chemical composition of the heart fractions resulted in statistically significant differences ($p < 0.05$) in the sensory assessment of the plum spirits (see Table 4). Both the distillation method and alcoholic strength of heart fractions affected the organoleptics of the obtained distillates. Also their associated effect was recorded ($p < 0.05$).

The sample obtained using double-stage distillation, with an alcohol by volume strength of 83%, gained the highest score. This plum brandy was characterized by delicate, pleasant, well

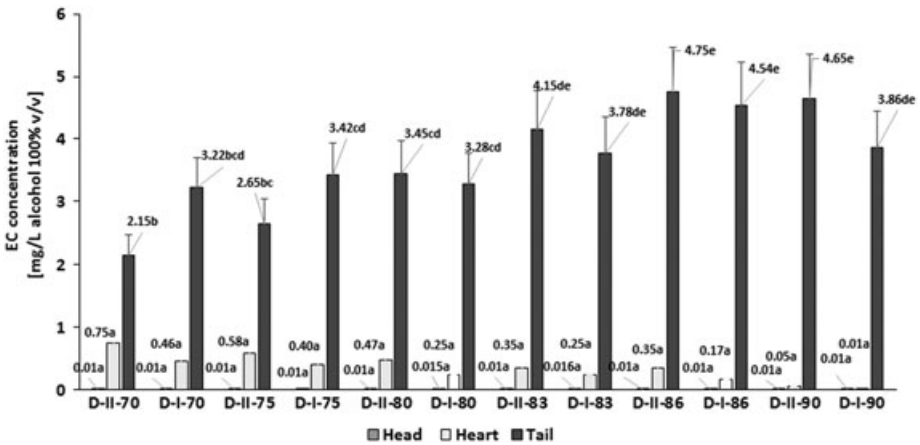



**Figure 4**. Ethyl carbamate distribution in fractions obtained during distillation of plum spirit. Means with different letters are significantly different ($p < 0.05$) as analysed by three-way ANOVA and the Tukey's *post-hoc* test.

**Table 4.** Sensory assessment of heart fractions from of plum distillate

| Heart fraction (% *v*/v) | Assessment characteristic | | | | |
|---|---|---|---|---|---|
| | Colour (max 2 pts) | Clearness (max 2 pts) | Odour (max 4 pts) | Taste (max 12 pts) | Total (max 20 pts) |
| *Two-stage distillation* | | | | | |
| 70 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $2.5^{ab} \pm 0.3$ | $7.2^{bcd} \pm 0.5$ | $13.7^{c} \pm 0.4$ |
| 75 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $2.8^{ab} \pm 0.2$ | $9.2^{ae} \pm 0.3$ | $16.7^{ab} \pm 0.3$ |
| 80 | 2.0a ± 0.0 | $2.0^{a} \pm 0.0$ | $3.2^{a} \pm 0.2$ | $10.5^{ef} \pm 0.2$ | $17.7^{b} \pm 0.2$ |
| 83 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $3.6^{a} \pm 0.2$ | $11.5^{f} \pm 0.5$ | $19.1^{f} \pm 0.3$ |
| 86 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $2.8^{ab} \pm 0.4$ | $9.0^{a} \pm 0.5$ | $15.8^{ad} \pm 0.4$ |
| 90 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $2.0^{b} \pm 0.5$ | $7.0^{BC} \pm 0.5$ | $13.0^{ce} \pm 0.5$ |
| *Single-stage distillation* | | | | | |
| 70 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $2.5^{ab} \pm 0.7$ | $7.2^{bcd} \pm 0.6$ | $13.7^{c} \pm 0.7$ |
| 75 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $2.8^{ab} \pm 0.5$ | $8.5^{ad} \pm 0.3$ | $15.3^{d} \pm 0.4$ |
| 80 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $3.0^{ab} \pm 0.2$ | $9.6^{ae} \pm 0.5$ | $16.6^{ab} \pm 0.4$ |
| 83 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $3.1^{ab} \pm 0.2$ | $10.5^{ef} \pm 0.3$ | $17.6^{b} \pm 0.4$ |
| 86 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $3.2^{a} \pm 0.5$ | $8.3^{acd} \pm 0.5$ | $15.5^{ad} \pm 0.5$ |
| 90 | $2.0^{a} \pm 0.0$ | $2.0^{a} \pm 0.0$ | $2.0^{b} \pm 0.5$ | $6.0^{b} \pm 0.5$ | $12.0^{e} \pm 0.5$ |

n.d., Not detected. Means in rows with different superscript lowercase letters are significantly different ($p < 0.05$) as analysed by two-way ANOVA and the Tukey's *post-hoc* test.

harmonized plum aroma and taste. Heart fractions from double-stage distillation with alcohol contents ranging from 75 to 80% *v*/v, and distillates produced by single-stage distillation with alcohol by volume strengths between 80 and 83% were also considered pleasant and acceptable in terms of taste and smell.

The highest amounts of volatile compounds in plum distillates with alcohol by volume strengths of 70% had negative effects on taste and aroma. The testers detected a sharp, acrid, solvent, pungent aroma and taste when compared with samples with higher alcohol content and as a consequence lower concentrations of volatiles. On the other hand, heart fractions with alcohol contents >86% *v*/v were assessed as sharp and burning, owing to the predominance of ethyl alcohol, which excessively reduced the concentrations of aroma components.

## Conclusions

The results of this study indicate that both double-stage and single-stage fractional distillation can be used to improve the chemical and organoleptic qualities of plum distillates. The composition of volatile components in the heart fractions of plum distillates varied greatly depending on the distillation methodology used (two-stage or single-stage), on the separation of the head fractions from the heart and on the final concentration of alcohol in the heart fractions. Increases in the alcohol by volume strength of the heart fractions (from 70 to 90% *v*/v) resulted in a gradual reduction in the concentrations of volatile compounds such as aldehydes, esters and higher alcohols, as well as in lower levels of methanol, HCN and EC.

The heart fraction with an alcohol content of 83% *v*/v obtained through the double-stage process received the highest scores from appraisers in terms of aroma and flavour. The distillates from single-stage distillation with alcohol contents between 80 and 83% *v*/v were also assessed as having pleasant aroma and taste. All the heart fractions contained methanol, HCN and EC in the concentrations much lower than the limits specified by EU regulation *(8)* for stone fruit distillates.

**Acknowledgements**

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