AROMATIC CHARACTERIZATION OF DISTILLATES WITH ADDED EXTRACTS OF HAWTHORN FLOWERS (*CRATAEGUS MONOGYNA – ROSACEAE*) AND HAWTHORN BERRIES (*CRATAEGUS MONOGYNA – FRUCTUS*)

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Abstract
Gas chromatographic study (GC-FID) to characterize the aromatic composition of distillates with added 50% and 70% ethanol extracts of hawthorn flowers (Crataegus monogyna - Rosaceae) and hawthorn berries (Crataegus monogyna - Fructus) was performed. The application of the extracts resulted in quantitative growth of total volatile compounds in part of the experimental variants. The incorporation of 50% hawthorn flowers ethanol extracts into the distillate was the most promising for enhancing its total volatile composition. Significant quantitative growth in the higher alcohols fraction was found when the same extracts were used. Four higher alcohols were dominant: 3-methyl-1-butanol, 2-methyl-1-butanol, 1-propanol and 2-butanol. 3-methyl-1-butanol was characterized by the highest amount. One aldehyde - acetaldehyde - has been found. The study proved that 50% ethanol extracts of hawthorn flowers and hawthorn berries were more promising in complicating of the ester composition, compared to 70% ethanol extracts. The main ester was ethyl acetate. Important esters found in the distillates were propyl acetate (second in quantitative presence), isopropyl acetate, isopentyl acetate, butyl acetate, ethyl butyrate, ethyl caprylate, phenyl acetate, ethyl hexanoate, ethyl decanoate. The methyl alcohol in all distillates was in the range of its normal presence. The application of hawthorn (flowers and berries) extracts led to an improvement of the terpene composition in the distillates, which enhanced their aromatic and biological potential.

Key words: hawthorn flowers (*Crataegus monogyna - Rosaceae*), hawthorn berries (*Crataegus monogyna - Fructus*), distillates, esters, higher alcohols, aldehydes, terpenes, methanol.

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INTRODUCTION

Hawthorn is a plant of the *Rosaceae* family. It is spread all over Bulgaria. The chemical composition of its flowers is rich and consist of various biologically active substances - hyperoside, acetylcholine, quercetin, essential oil, organic acids and tannins, flavonoids, carotenoids, choline (Landjev, 2005). Its berries (*Fructus Crataegi oxyacanthae*) ripen in the period August-September and also contain a number of biologically active components - flavonoids, citric acid, tannins, pectin and others (Landjev, 2005). Due to the proven bioactivity compounds, extracts of this plant have the potential to be added to various nutritional matrices, such as distilled spirits.

The groups of compounds that influence the aroma formation in higher alcohol distilled beverages are esters, higher alcohols, aldehydes and terpene compounds (Kostik et al., 2014; Marku et al., 2015; Yankov et al., 2000). A number of studies have been conducted on the aromatic characterization of distillates.

Coldea et al. (2011) conducted a study to identify the major volatile compounds in three traditional Romanian fruit brandies - plum, apple and pear. The team found the presence of 1-propanol, 2-butanol, isobutyl alcohol, amyl-active alcohol, isoamyl alcohol and 1-butanol (higher alcohols); ethyl acetate (esters), acetaldehyde and furfural (aldehydes). Tesevic et al. (2009) characterized the volatile composition of cherry fruit brandy. The team found the main presence of 1-propanol, 2-methyl-1-propanol, 1-butanol, amyl alcohols, 1-hexanol (higher alcohols), phenylethanol (aromatic alcohol), ethyl acetate (esters) and acetaldehyde (aldehydes). Kostik et al. (2014) conducted a study on the volatile fraction of grapes and plum distillates. For both distillate groups, the dominant presence of higher alcohols - n-propyl, isobutyl and isoamyl, was found.

The question of the presence of methyl alcohol in distillates is important. This compound is formed from the fruit pectin, which is hydrolyzed to methanol via the pectolytic enzyme complex of the fruit (Marinov, 2005; Lukic et al., 2011;). It is toxic (in higher concentrations) and varies in distillates in the range of 400.00 – 2000.00 mg/dm^3.

The aim of this study is to perform aromatic characterization of wine distillates with added hawthorn flowers (*Crataegus monogyna - Rosaceae*) and hawthorn berries (*Crataegus monogyna - Fructus*) extracts.

MATERIALS AND METHODS

Plant sources, fermentation, distillation and preparation of the extracts

The 50% and 70% ethanol extracts of hawthorn flowers (*Crataegus monogyna – Rosaceae*) and hawthorn berries (*Crataegus monogyna - Fructus*) were used as the plant source for incorporation into the distillate. The hawthorn is from the *Rosaceae* family. It is distributed between various shrubs and mixed forests, up to 1500 m above sea level, throughout Bulgaria. It is a prickly shrub or small tree up to 5 m high. The leaves are cut into 3-7 lobes and serrated. Above are shiny and darker green, below - light green, fibrous. The flowers are white, with thyroid inflorescences, with a 5-lobed cup, a 5-leaf garland and many stamens. The berries are stone. The flowers are used before their full bloom (April-May); the berries ripen in August – October. They are red to orange-yellow, 6-8 mm in diameter, ovate-like or almost spherical with one oval stone. The berries (*Fructus Crataegi oxyacanthae*) are harvested when fully ripe, but before they begin to soften (Landjev, 2005).

The plant sources (hawthorn berries and hawthorn flowers) were collected from Bulgaria, District Blagoevgrad, near Satovcha, Locality Aspen.

Geogr. coord. (35TKG 57029 12827), June. degr.	
Lat. 41.62944	**Lon.** 24.50992
UTM/MGRS KG51 **Leg.:** A. Parzhanova	**Altitude** 1134 m
Det.: A. Parzhanova	

The raw material was ground into an electric robot. Six fractions with different diameter of ground particles of hawthorn flowers (*Crataegus monogyna - Rosaceae*) and hawthorn berries (*Crataegus monogyna - Fructus*) were obtained:

Class I $\frac{132}{0}$ μm - 13,23 %;

Class II $\frac{280}{132}$ μm -23,43 %;

Class III $\frac{450}{280}$ μm -17,15 %;

Class IV $\frac{670}{450}$ μm -14,56 %;

Class V $\frac{1000}{670}$ μm -17,37 %;

Class VI $\frac{2000}{1000}$ μm- 14,26 %.

The ethanol extracts were prepared by pouring 1 g of the ground plant raw material (hawthorn flowers and berries) with 20 ml of 50% ethanol and subsequently extracting using 70% ethanol in the same ratio. The purity of the ethanol used was 95%. The ratio of plant source: ethanol was calculated according to the production need of the required amounts of extract for incorporation into the distillates. The solutions prepared were stored at 18-20 ° C in the dark for 14 days. This is the period during which good contact was made for maximum extraction. Then the extracts were filtered and stored at 0 - 4° C.

To obtain the distillate, grapes of the Melnik-55 variety cultivated in the area of Polski Trambesh village, Sandanski region, Blagoevgrad was used. 600 kg grapes was used from which 80 liters of distillate with 63 vol. % alcohol have been obtained. The grapes were subjected to a fermentation process in accordance with the classical scheme for the production of dry red wines: Crushing and Destemming ► Sulphitation (50 mg/kg SO_2) ► Alcoholic fermentation (dry wine yeasts *Saccharomyces cerevisiae* 20 g/hl; temperature 28° C) ► Separation from solids ► Further Sulphitation ► Storage (Yankov, 1992).

The distillation was carried out in the licensed "Dennis-Marian Trenev Distillery 2008" Ltd., Novo Delchevo, Sandanski, Bulgaria. From the distillate obtained, experimental samples were prepared by adding (into the distillate) 50% and 70% ethanol extracts of hawthorn flowers (*Crataegus monogyna - Rosaceae*) and hawthorn berries (*Crataegus monogyna - Fructus*) in quantities of 20, 50, 80, 100, 200, 400 and 600 ml. Pure distillate without extracts was used as a control sample.

Determination of ethanol content of the obtained distillates

The ethanol content of the obtained distillates was defined by specialized equipment with high precision – automatic distillation unit - DEE Destillation Unit with Densimat and Alcomat, Gibertini, Milan, Italy.

Volatile content determination by GC-FID

Gas chromatographic determination of the volatile components in distillates was done. The content of major volatile compounds was determined on the basis of stock standard solution prepared in accordance with the IS method 3752:2005. The method describes the preparation of standard solution with one congener, but the step of preparation was followed for the preparation of a solution with more compounds. The standard solution in this study included the compounds with purity > 99.0%. The 2 µl of prepared standard solution was injected in gas chromatograph Varian 3900 (Varian Analytical Instruments, Walnut Creek, California, USA) with a capillary column VF max MS (30 m, 0.25 mm ID, DF = 0.25 µm), equipped with a flame ionization detector (FID). The used carrier gas was He. Hydrogen to support combustion was supplied to the chromatograph via a hydrogen bottle. The injection was manually by microsyringe.

The parameters of the gas chromatographic determination were: injector temperature – 220 °C; detector temperature – 250 °C, initial oven temperature – 35 °C/retention 1 min, rise to 55 °C with step of 2 °C/min for 11 min, rise to 230 °C with step of 15 °C/min for 3 min. Total time of chromatography analysis – 25.67 min. The identified retention times of the compounds in the standard solution were: acetaldehyde (3.141), ethyl acetate (3.758), methanol (3.871), 2-propanol (5.170), isopropyl acetate (5.975), 1–propanol (6.568), 2–butanol (7.731), propyl acetate (9.403), 2–methyl-propanol (10.970), 1–butanol (11.509), isobutyl acetate (11.662), ethyl butyrate (12.710), butyl acetate (12.752), 2–methyl-1-butanol (13.054), 4-methyl-2-pentanol (13.629), 3–methyl-1–butanol (13.840), 1–pentanol (15.180), isopenthyl acetate (15.965), pentyl acetate (16.033), 1–hexanol (16.276), ethyl hexanoate (16.376), hexyl acetate (16.510), 1–heptanol (16.596), linalool oxide (16.684), phenyl acetate (18.055), ethyl caprylate (18.625), α-terpineol (19.066), 2-phenyl ethanol (19.369), nerol (19.694), β-citronellol (19.743), geraniol (19.831), ethyl decanoate (19.904). As an internal standard octanol was used.

After determination of the retention times of the compounds in the standard solution the identification and quantification of the volatile substances in the distillates was done. The volatile composition was determined based on direct injection of the distillates. Prepared samples were injected in an amount of 2 µl in a gas chromatograph and was carried out an identification and quantification of the substances in each of them.

Statistical processing

Statistical analysis of the data was performed by determining the standard deviation (± SD), with triplicate. It was made using Excel 2007 from the Microsoft Office Package (Microsoft Corporation, USA).

RESULTS AND DISCUSSION

The results of the established volatile composition in the control distillate and distillates with added hawthorn flowers (*Crataegus monogyna - Rosaceae*) and hawthorn berries (*Crataegus monogyna - Fructus*) extracts (50% and 70%) are presented in Tables 1 - 4.

Considering the total amount of volatile compounds found in the control and experimental distillates using 50% ethanol hawthorn flowers extracts, a high final concentration of volatile compounds was found at 1000:50 (2564.94 ± 45.52 mg/dm^3), 1000:20 (2483.59 ± 30.38 mg/dm^3) and 1000:400 (4463.53 ± 64.56 mg/dm^3) compared to the control sample (1962.97 mg/dm^3). The volatile fraction in the 1000:400 variant was clearly higher, more than twice from that found in the control variant. When 70% ethanol hawthorn flowers extract was used, only one variant was distinguished - 1000:50 (2084.33 ± 38.96 mg/dm^3), shown a total volatile compound content higher than the control (1962.97 ± 3.62 mg/dm^3).

When 50% hawthorn berries ethanol extracts were applied, all established volatile compounds were lower than the control. The range of total volatile composition whit using of these extracts (347.93 ± 7.34 mg/dm^3 - 1761.83 ± 21.78 mg/dm^3) was lower than the control content (1962.97 ± 3.62 mg/dm^3).

With the application of 70% ethanol hawthorn berries extracts, only variant 1000:50 (2854.84 ± 18.78 mg/dm^3) shown a total amount of volatile compounds higher than the control.

Comparing the two sources of hawthorn extract (flowers and berries), it can be stated that the extraction of hawthorn flowers with 50% ethanol resulted in significant quantitative growth of the total volatile compounds in three experimental variants (1000:50; 1000:200 1000:400), which made these extracts promising in increasing of the quantitative volatile content of the distillates obtained.

At the control sample a total amount of higher alcohols - 1301.28 ± 1.89 mg/dm^3 was found. When 50% ethanol hawthorn flowers extracts were used, significantly higher levels of higher alcohols were reported in the 1000:50 (2083.99 ± 22.32 mg/dm^3), 1000:200 (2123.18 ± 23.01 mg/dm^3) and 1000:400 variants (3953.75 ± 45.62 mg/dm^3). When 70% ethanol extracts from the same source were used, no increased final higher alcohol content was observed in the experimental variants. All quantities under this indicator were lower than the control.

The application of 50% hawthorn berries ethanol extracts shown the detected amounts of higher alcohols ranged from 243.15 ± 3.70 mg/dm^3 to 1257.74 ± 8.42 mg/dm^3. These quantities were lower than the control (1301.28 ± 1.89 mg/dm^3). The incorporation of 50% hawthorn berries ethanol extracts was not reflected in increased final levels of higher alcohols. When 70% hawthorn berries ethanol extracts were used, a markedly higher amount of higher alcohols than the control was found only in variant 1000:50 (2313.11 ± 10.24 mg/dm^3). All other variants shown concentrations lower than the control at this indicator.

The results obtained shown a promising source of 50% hawthorn flowers ethanol extracts, led to significant growth in the final amount of higher alcohols in the distillates. This increased their complexity and was a prospect for future ester formation by the eventual aging process of the distillates obtained.

The group of higher alcohols in the experimental variants of 50% and 70% ethanol extracts of hawthorn flowers and hawthorn berries were dominated by 2-methyl-1-butanol, 3-methyl-1-butanol, 1-propanol and 2-butanol. At the highest concentration of this group 3-methyl-1-butanol was distinguished. Its variation in the samples with added 50% ethanol hawthorn flowers extracts ranged from 225.10 ± 1.78 mg/dm^3 - 1334.17 ± 9.98 mg/dm^3. Only two of the samples shown quantities of this component (1000:200 - 1334.17 ± 9.98 mg/dm^3; 1000:400 - 1081.72 ± 9.78 mg/dm^3) higher than that found in the control (831.95 ± 0.15 mg/dm^3). In the samples with the application of 70% ethanol hawthorn flowers extracts, 3-methyl-1-butanol was in the range of 115.49 ± 8.25 mg/dm^3 - 1047.58 ± 5.64 mg/dm^3, with only two variants (1000:20 and 1000:50) with concentrations higher than the control. Lower concentrations of this major component of higher alcohols were noticeable in the variants with 70% hawthorn flowers ethanol extracts applied, compared to those using 50% ethanol plant extracts. The data on the concentration of 3-methyl-1-butanol correlated with the observed normal amounts, according to Velkov, 1996.

3-methyl-1-butanol shown the highest quantitative dominance too in the variants with 50% and 70% ethanol extracts of hawthorn berries. For the applied 50% ethanol extracts it varied from 149.50 ± 1.17 mg/dm^3 - 822.24 ± 4.85 mg/dm^3, and for the used 70% ethanol extracts from 209.27 ± 3.42 mg/dm^3 - 1473.34 ± 4.69 mg/dm^3. In the experimental variants with added 50% ethanol hawthorn berries extracts, all amounts of 3-methyl-1-butanol were lower than the control (831.95 ± 0.15 mg/dm^3), whereas when 70% ethanol extracts were applied it differed only one variant 1000:50 (1473.34 ± 4.69 mg/dm^3) with a concentration of this higher alcohol higher than the control. The established amounts of major higher alcohols correlated with the identified major representatives in other distillate studies (Tesevic et al., 2009 Kostik et al., 2014).

In some of the distillates, a number of important representatives of the higher alcohols group - 4-methyl-2-pentanol, 2-propanol, 2-methyl-1-propanol, 1-pentanol, 1-hexanol, have been found in smaller quantities. In some of the variants, the aromatic alcohol, 2-phenylethanol, has also been identified. It is characterized by a typical rose aroma (Chobanova, 2012).

From the aldehydes group in all distillates the main representative - acetaldehyde - was found. At normal concentrations (50.00 - 300.00 mg/dm^3), it imparts a fruity aroma to the alcoholic beverages, but when it exceeds its threshold values, it has a negative effect, characterized by an oxidized taste-aromatic tone (Velkov, 1996).

In the experimental variants with added 50% ethanol hawthorn flowers extracts, it was found in a larger amount (67.07 ± 2.32 mg/dm^3) than the control (54.72 ± 0.25 mg/dm^3) only in the 1000:20 variant. Its levels were at the norm for its positive influence on the aromatic quality.

The acetaldehyde concentrations ranged from 0.05 ± 0.01 mg/dm^3 - 53.59 ± 1.56 mg/dm^3 when 70% ethanol hawthorn flowers extracts were applied. All concentrations of this main aldehyde in these experimental variants were lower than the control.

When 50% ethanol extracts of hawthorn berries were applied, acetaldehyde varied in the experimental variants from 0.05 ± 0.01 mg/dm^3 - 116.63 ± 3.17 mg/dm^3. Only one of the samples (1000:600) showed the acetaldehyde concentration (116.63 ± 3.17 mg/dm^3) higher than the control (54.72 ± 0.25 mg/dm^3). When 70% ethanol extracts of hawthorn berries were applied, acetaldehyde ranged from 11.07 ± 0.89 mg/dm^3 - 45.73 ± 0.37 mg/dm^3. In all experimental variants, its levels were lower than that established in the control variant.

The acetaldehyde concentrations found in all analyzed samples from the two experimental groups corresponded to the normal amounts of this aldehyde in distillates, according to Velkov, 1996.

The esters are components of the volatile composition that exert the strongest influence on the expression of various aromatic nuances.

When 50% hawthorn flowers ethanol extracts were applied, the total ester content between the experimental variants ranged from 48.25 ± 1.13 mg/dm^3 - 1079.98 ± 17.07 mg/dm^3, and when 70% ethanol hawthorn flowers extracts were applied this concentrations was in the range of 56.71 ± 1.19 mg/dm^3 - 443.34 ± 17.74 mg/dm^3.

In the experimental group of 50% hawthorn flowers ethanol extract applied, the total ester content of variants 1000:50 (1079.98 ± 17.07 mg/dm^3) and 1000:200 (360.31 ± 1.91 mg/dm^3) exceeded the ester concentration of the control (242.18 ± 1.15 mg/dm^3). With the used 70% ethanol hawthorn flowers extracts, only one variant, 1000:20, shown a total ester concentration (443.34 ± 17.74 mg/dm^3) higher than the control.

Comparing the two groups of experimental variants, it can be seen that the group with applied 50% hawthorn flowers ethanol extracts showed higher final ester levels compared to that of 70% hawthorn flowers ethanol extracts. The 50% ethanol extracts were a better prospect of complicating the ester composition of distillates.

When 50% ethanol hawthorn berries extract was applied, two of the experimental variants 1000:80 and 1000:600 shown a total ester content (422.59 ± 3.00 mg/dm^3; 382.99 ± 6.53 mg/dm^3, respectively) higher than the control (242.18 ± 1.15 mg/dm^3). With the application of 70% hawthorn berries ethanol extracts, the total ester content in the experimental variants ranged from 58.70 ± 2.84 mg/dm^3 - 163.37 ± 3.44 mg/dm^3 and all total ester levels were lower than the control. In this experimental group, 50% ethanol extracts provide a better perspective on the complexity of the ester composition.

The basic ester identified in all experimental variants was ethyl acetate. In the control sample it was found in concentration of 242.08 ± 1.12 mg/dm^3. According to Velkov (1996) in distillates the ester must move in the concentration range 420.00 - 700.00 mg/dm^3. At this concentration, it exerts a positive influence on the aromatic profile of the distillate. The variation of the ester found in the different experimental variants was as follows:

● When 50% ethanol hawthorn flowers extracts were applied - 48.10 ± 1.10 mg/dm^3 - 344.15 ± 1.63 mg/dm^3;

● When 70% ethanol hawthorn flowers extracts were applied - 36.34 ± 0.29 mg/dm^3 - 143.83 ± 4.44 mg/dm^3;

● When 50% hawthorn berries ethanol extracts were applied - 20.28 ± 0.64 mg/dm^3 - 133.03 ± 1.21 mg/dm^3;

● When 70% hawthorn berries ethanol extracts were applied - 42.22 ± 2.10 mg/dm^3 - 112.82 ± 1.93 mg/dm^3.

The concentrations of ethyl acetate in all experimental variants correlated with the ranges of its normal quantitative presence in distillates. This was evidence of the positive impact it has on the fruity-aromatic profile of the distillates.

The other esters were at lower levels. They were identified as representatives at different levels of presence and quantification. Important esters found in the distillates were propyl acetate (second in quantitative presence), isopropyl acetate, isopentyl acetate, butyl acetate, ethyl butyrate, ethyl caprylate, phenyl acetate, ethyl hexanoate, ethyl decanoate.

The methyl alcohol is a compound which determines, on the one hand, the authenticity of the distillate (factor - fruit raw material) and, on the other, the degree of its safety, since at higher levels the methanol has a strong toxic potential. Velkov (1996) determined the variation of methanol content in distillates from 400.00 - 2000.00 mg/dm^3. Methyl alcohol was identified in the control sample at 364.74 ± 0.32 mg/dm^3. Its variation found in the experimental variants was the following:

● When 50% ethanol hawthorn flowers extracts were applied - 95.74 ± 2.45 mg/dm^3 - 525.73 ± 3.12 mg/dm^3;

● When 70% ethanol hawthorn flowers extracts were applied - 17.98 ± 1.85 mg/dm^3 - 284.41 ± 6.85 mg/dm^3;

● When 50% hawthorn berries ethanol extracts were applied - 57.73 ± 1.65 mg/dm^3 - 413.21 ± 2.19 mg/dm^3;

● When 70% ethanol extracts of hawthorn berries were applied - 69.59 ± 1.12 mg/dm^3 - 346.49 ± 3.56 mg/dm^3.

All methanol levels found were in the range of its normal presence, preventing its toxic potential. It is noteworthy that in the variants of the applied 50% and 70% ethanol hawthorn flowers extracts, the distillates with incorporated 70% hawthorn flowers ethanol extracts shown lower methyl alcohol levels. This resulted in better methanol purity in these experimental variants.

The terpene fraction in the variants was represented by 5 identified terpene alcohols - α-terpineol, β-citronellol, linalool oxide, nerol and geraniol. They are a major terpene representative in the fermented alcoholic beverages (Lengyel, 2012). The total terpene content of the control sample was 0.05 ± 0.01 mg/dm^3, represented by the only one identified terpen - geraniol.

In the experimental variants with incorporated 50% ethanol hawthorn flowers extracts in variants 1000:50 and 1000:80 terpenes have not been established. In all other variants, the total terpene content was higher than the control content and ranged from 0.10 ± 0.02 mg/dm^3 - 0.23 ± 0.03 mg/dm^3.

When 70% ethanol hawthorn flowers extracts were applied only in variant 1000:20, a total terpene concentration was similar to the observed in the control. In all other variants of this experimental group the total terpene content (0.10 ± 0.02 mg/dm^3 - 0.18 ± 0.09 mg/dm^3) was higher than that of the control sample

Table 1. Volatile compounds identified in the control (distillate) and experimental samples with the addition of 50% ethanol hawthorn flowers (*Crataegus monogyna* - *Rosaceae*) extracts

IDETIFIED COMPOUNDS, mg/dm³		**DISTILLATES WITH ADDED ETHANOL EXTRACTS (50%) FROM PLANT SOURCES**						
	DISTILLATE CONTROL	HAWTHORN FLOWER 1000:20	HAWTHORN FLOWER 1000:50	HAWTHORN FLOWER 1000:80	HAWTHORN FLOWER 1000:100	HAWTHORN FLOWER 1000:200	HAWTHORN FLOWER 1000:400	HAWTHORN FLOWER 1000:600
Ethyl alcohol, vol.%	68.84	66.62	66.18	67.44	66.06	64.50	59.10	57.18
Acetaldehyde	54.72±0.25	29.67±1.12	23.55±0.89	27.59±0.15	25.00±1.00	67.07±2.32	40.14±7.25	14.23±0.21
Methanol	364.74±0.32	240.05±4.25	467.42±5.24	312.92±0.17	162.47±3.12	525.73±3.12	340.26±9.86	95.74±2.45
2-methyl-1-butanol	190.38±0.12	163.76±2.11	158.92±6.89	104.37±0.24	92.31±4.65	309.59±4.15	249.60±8.64	51.53±3.54
3-methyl-1-butanol	831.95±0.15	695.07±9.16	687.62±2.87	456.70±0.68	412.44±6.87	1334.17±9.98	1081.72±9.78	225.10±1.78
4-methyl-2-pentanol	ND	0.05±0.01	ND	ND	0.05±0.01	0.05±0.01	0.05±0.01	0.05±0.01
1-propanol	33.89±0.56	27.52±0.89	25.31±0.98	18.73±1.12	17.26±1.10	54.53±0.45	40.37±7.12	9.35±0.87
2-propanol	ND	0.05±0.01	ND	ND	ND	0.05±0.01	0.05±0.01	0.05±0.01
2-butanol	ND	206.65±10.12	212.14±11.58	137.53±2.11	130.00±0.99	405.59±7.82	301.91±10.27	66.52±4.25
2-methyl-1-propanol	245.01±1.05	0.05±0.01	ND	0.05±0.01	0.05±0.01	0.05±0.01	2256.90±9.18	0.05±0.01
1-hexanol	ND	0.05±0.01	ND	ND	0.05±0.01	19.10±0.57	ND	0.05±0.01
2-phenylethanol	ND	0.05±0.01	ND	ND	ND	0.05±0.01	23.15±0.61	19.56±0.39
Total higher alcohols	***1301.28±1.89***	***1093.25±22.33***	***1083.99±22.32***	***717.38±4.16***	***652.16±13.64***	***2123.18±23.01***	***3953.75±45.62***	***372.26±10.87***
Ethyl acetate	242.08±1.12	149.61±0.12	230.58±12.24	126.98±***4.65***	116.55±1.14	344.15±1.63	129.13±1.78	48.10±1.10
Propyl acetate	ND	ND	849.35±4.78	ND	ND	ND	ND	ND
Isopropyl acetate	ND	0.05±0.01	ND	ND	ND	0.05±0.01	ND	ND
Isopentyl acetate	ND	ND	ND	ND	ND	ND	0.05±0.01	0.05±0.01
Isobutyl acetate	ND	ND	ND	ND	ND	ND	0.05±0.01	ND
Ethyl butyrate	ND	0.05±0.01	ND	0.05±0.01	0.05±0.01	0.05±0.01	ND	0.05±0.01
Ethyl caprylate	0.05±0.02	0.05±0.01	ND	0.05±0.01	ND	0.05±0.01	ND	ND
Ethyl hexanoate	ND	ND	ND	ND	ND	ND	0.05±0.01	ND
Phenyl acetate	ND	9.22±0.12	ND	0.05±0.01	0.05±0.01	16.01±0.25	ND	0.05±0.01
Ethyl decanoate	0.05±0.01	ND	0.05	0.05±0.01	ND	ND	ND	ND
Total esters	***242.18±1.15***	***158.98±0.27***	***1079.98±17.07***	***127.18±4.69***	***116.65±1.16***	***360.31±1.91***	***129.28±1.81***	***48.25±1.13***
α – terpineol	ND	0.05±0.01	ND	ND	0.05±0.01	ND	ND	0.05±0.01
Nerol	ND	0.05±0.01	ND	ND	0.05±0.01	ND	0.05±0.01	ND
β – citronellol	ND	0.05±0.01	ND	ND	0.05±0.01	0.05±0.01	ND	0.05±0.01
Geraniol	0.05±0.01	0.05±0.01	ND	ND	0.05±0.01	0.05±0.01	0.05±0.01	0.13±0.01
Total terpenes	***0.05±0.01***	***0.20±0.04***	-	-	***0.20±0.04***	***0.10±0.02***	***0.10±0.02***	***0.23±0.03***
TOTAL CONTENT	***1962.97±3.62***	***1522.15±28.01***	***2654.94±45.52***	***1185.07±9.66***	***956.48±18.96***	***2483.59±30.38***	***4463.53±64.56***	***530.71±14.69***

Table 2. Volatile compounds identified in the experimental samples with the addition of 70% ethanol hawthorn flowers (*Crataegus monogyna - Rosaceae*) extracts

IDETIFIED COMPOUNDS, mg/dm^3	DISTILLATES WITH ADDED ETHANOL EXTRACTS (70%) FROM PLANT SOURCES						
	HAWTHORN FLOWER 1000:20	HAWTHORN FLOWER 1000:50	HAWTHORN FLOWER 1000:80	HAWTHORN FLOWER 1000:100	HAWTHORN FLOWER 1000:200	HAWTHORN FLOWER 1000:400	HAWTHORN FLOWER 1000:600
Ethyl alcohol, vol.%	68.28	68.58	68.32	68.76	69.80	69.10	69.78
Acetaldehyde	10.55±0.12	53.59±1.56	28.26±1.10	0.05±0.01	12.32±1.14	40.49±0.84	30.00±1.14
Methanol	174.55±8.12	284.41±6.85	157.41±0.99	114.73±5.55	64.54±2.45	17.98±1.85	146.12±5.14
2-methyl-1-butanol	212.80±9.14	209.82±8.24	107.38±9.87	105.21±0.34	35.25±0.56	25.48±0.85	76.16±3.10
3-methyl-1-butanol	856.39±7.45	1047.58±5.64	505.25±8.96	125.53±0.26	168.77±8.96	115.49±8.25	344.16±9.84
4-methyl-2-pentanol	0.05±0.01	0.05±0.01	ND	ND	0.05±0.01	ND	ND
1-propanol	24.02±0.23	36.07±0.12	18.61±0.45	0.05±0.01	6.78±0.78	0.05±0.01	14.58±1.11
2-propanol	0.05±0.01	0.05±0.01	0.05±0.01	ND	10.37±1.12	ND	0.05±0.01
2-butanol	35.03±2.65	272.23±10.29	137.19±6.54	67.31±0.12	51.69±2.12	0.05±0.01	103.42±5.45
1- butanol	0.05±0.01	ND	ND	ND	ND	ND	ND
1-pentanol	9.89±0.87	ND	ND	ND	ND	ND	ND
1-hexanol	0.05±0.01	ND	ND	ND	ND	ND	ND
2-phenylethanol	0.05±0.01	ND	ND	ND	7.49±0.24	13.25±0.45	21.12±0.87
Total higher alcohols	***1138.38±20.39***	***1565.80±24.31***	***768.48±25.83***	***192.89±0.73***	***280.40±13.79***	***154.32±9.57***	***559.49±20.38***
Ethyl acetate	64.36±7.14	143.83±4.44	77.25±2.11	73.47±0.88	41.39±0.65	36.34±0.29	96.45±7.42
Propyl acetate	364.90±9.63	ND	0.05±0.01	ND	0.05±0.01	ND	ND
Isopropyl acetate	0.05±0.01	ND	ND	ND	ND	ND	ND
Isopentyl acetate	ND	0.05±0.01	ND	ND	ND	ND	ND
Isobutyl acetate	ND	ND	ND	ND	ND	27.63±2.12	ND
Ethyl hexanoate	ND	0.05±0.01	0.05±0.01	ND	15.22±0.52	ND	13.02±0.98
Phenyl acetate	4.44±0.27	9.20±0.64	ND	ND	0.05±0.01	ND	0.05±0.01
Ethyl decanoate	9.59±0.69	27.25±1.11	0.05±0.01	0.05±0.01	ND	0.05±0.01	0.05±0.01
Total esters	***443.34±17.74***	***180.38±6.21***	***77.40±2.14***	***73.52±0.89***	***56.71±1.19***	***64.02±2.42***	***109.57±8.42***
α – terpineol	ND	0.05±0.01	ND	ND	0.05±0.01	ND	ND
Nerol	ND	ND	ND	ND	0.05±0.01	ND	0.05±0.01
β – citronellol	ND	0.05±0.01	0.05±0.01	0.05±0.01	ND	0.05±0.01	ND
Geraniol	0.05±0.01	0.05±0.01	0.05±0.01	0.05±0.01	0.05±0.01	0.13±0.08	0.05±0.01
Total terpenes	***0.05±0.01***	***0.15±0.03***	***0.10±0.02***	***0.10±0.02***	***0.15±0.03***	***0.18±0.09***	***0.10±0.02***
TOTAL CONTENT	***1766.87±46.38***	***2084.33±38.96***	***1031.65±30.08***	***381.29±7.54***	***414.12±18.60***	***276.99±14.77***	***845.28±35.10***

Table 3. Volatile compounds identified in the experimental samples with the addition of 50% ethanol hawthorn berries (*Crataegus monogyna - Rosaceae*) extracts

IDETIFIED COMPOUNDS, mg/dm^3	DISTILLATES WITH ADDED ETHANOL EXTRACTS (50%) FROM PLANT SOURCES						
	HAWT.BER. 1000:20	HAWT.BER. 1000:50	HAWT.BER. 1000:80	HAWT.BER. 1000:100	HAWT.BER. 1000:200	HAWT.BER. 1000:400	HAWT.BER. 1000:600
Ethyl alcohol, vol.%	69.00	67.26	64.58	66.46	63.84	58.86	55.64
Acetaldehyde	12.47±0.98	23.51±0.41	0.05±0.01	40.96±0.15	8.01±0.12	19.77±0.47	116.63±3.17
Methanol	100.90±1.21	172.75±2.10	413.21± 2.19	264.67±1.36	57.73±1.65	118.27±2.14	142.19±1.56
2-methyl-1-butanol	63.60±1.80	127.47±1.85	76.94±2.65	184.43±1.87	34.87±0.45	72.51±1.65	156.10±1.47
3-methyl-1-butanol	280.91±0.95	561.24±4.23	332.49±3.24	822.24±4.85	149.50±1.17	392.89±3.89	664.51±4.12
4-methyl-2-pentanol	0.05±0.01	0.05±0.01	ND	0.05±0.01	0.05±0.01	0.05±0.01	ND
1-propanol	11.18±0.65	19.30±0.91	12.76±0.47	30.75±0.54	5.90±0.14	12.96±1.19	26.33±1.10
2-propanol	0.05±0.01	0.05±0.01	ND	0.05±0.01	0.05±0.01	0.05±0.01	ND
2-butanol	81.27±1.54	141.39±0.23	96.87±0.38	220.12±1.12	43.62±094	93.72±2.14	198.80±2.16
2-methyl-1-propanol	0.05±0.01	0.05±0.01	ND	0.05±0.01	0.05±0.01	0.05±0.01	ND
1-pentanol	ND	ND	ND	ND	5.40±0.32	ND	0.05±0.01
1-hexanol	ND	0.05±0.01	ND	0.05±0.01	ND	47.07±2.89	36.78±0.69
2-phenylethanol	0.05±0.01	0.05±0.01	ND	ND	3.71±0.65	72.29±1.53	36.89±0.84
Total higher alcohols	***437.16±4.98***	***849.65±7.27***	***519.06±6.74***	***1257.74±8.42***	***243.15±3.70***	***691.59±13.32***	***1119.46±10.39***
Ethyl acetate	65.94±0.62	121.17±1.15	73.34±0.85	133.03±1.21	32.25±0.87	20.28±0.64	116.32±0.98
Propyl acetate	ND	ND	349.20±2.14	ND	ND	ND	0.05±0.01
Isopropyl acetate	ND	0.05±0.01	ND	ND	ND	ND	ND
Isopentyl acetate	ND	ND	ND	0.05±0.01	ND	21.87±0.31	38.23±1.74
Butyl acetate	ND	ND	ND	0.05±0.01	ND	ND	ND
Ethyl butyrate	0.05±0.01	0.05±0.01	0.05±0.01	0.05±0.01	ND	ND	ND
Ethyl caprylate	ND	0.05±0.01	ND	0.05±0.01	ND	ND	0.05±0.01
Phenyl acetate	ND	ND	ND	0.05±0.01	ND	0.05±0.01	55.27±0.96
Phenyl acetate	ND	7.43±0.74	ND	11.71±1.28	ND	ND	34.17±0.83
Ethyl hexanoate	ND	ND	ND	ND	ND	ND	30.81±0.89
Ethyl decanoate	ND	ND	ND	0.05±0.01	6.69±0.98	ND	108.09±1.11
Total esters	***65.99±0.63***	***128.75±1.92***	***422.59±3.00***	***145.04±2.55***	***38.94±1.85***	***42.20±0.96***	***382.99±6.53***
Linalool oxide	ND	ND	ND	ND	ND	ND	0.05±0.01
α – terpineol	ND	0.05±0.01	ND	0.05±0.01	ND	0.05±0.01	0.05±0.01
Nerol	ND	ND	ND	ND	0.05±0.01	ND	0.05±0.01
β – citronellol	ND	0.05±0.01	ND	0.05±0.01	ND	0.05±0.01	0.41±0.10
Geraniol	0.05±0.01	0.05±0.01	ND	0.05±0.01	0.05±0.01	0.20±0.09	ND
Total terpenes	***0.05±0.01***	***0.15±0.03***	-	***0.15±0.03***	***0.10±0.02***	***0.30±0.11***	***0.56±0.13***
TOTAL CONTENT	***616.57±7.81***	***1174.81±11.73***	***1354.86±11.94***	***1708.56±12.51***	***347.93±7.34***	***872.13±17.00***	***1761.83±21.78***

Table 4. Volatile compounds identified in the experimental samples with the addition of 70% ethanol hawthorn berries (*Crataegus monogyna - Rosaceae*) extracts

IDETIFIED COMPOUNDS, mg/dm^3	DISTILLATES WITH ADDED ETHANOL EXTRACTS (70%) FROM PLANT SOURCES						
	HAWT.BER. 1000:20	HAWT.BER. 1000:50	HAWT.BER. 1000:80	HAWT.BER. 1000:100	HAWT.BER. 1000:200	HAWT.BER. 1000:400	HAWT.BER. 1000:600
Ethyl alcohol, vol.%	67.20	68.24	68.26	68.98	67.04	68.46	68.66
Acetaldehyde	11.07±0.89	31.35±1.45	21.80±0.47	20.90±0.68	19.08±0.63	29.22±0.34	45.73±0.37
Methanol	69.59±1.12	346.49±3.56	120.30±1.73	151.25±2.16	130.86±1.10	147.67±2.83	200.00±1.24
2-methyl-1-butanol	44.78±1.25	359.29±2.17	57.18±0.59	77.95±1.98	137.60±0.65	82.43±3.98	129.68±2.11
3-methyl-1-butanol	209.27±3.42	1473.34±4.69	268.22±2.69	363.52±3.59	503.28±4.26	494.99±0.67	694.62±2.65
4-methyl-2-pentanol	0.05±0.01	ND	ND	ND	0.05±0.01	0.05±0.01	0.05±0.01
1-propanol	8.09±0.19	52.83±0.63	12.33±0.84	15.26±0.52	17.53±0.24	15.50±0.67	23.25±0.73
2-propanol	0.05±0.01	0.05±0.01	ND	0.05±0.01	0.05±0.01	0.05±0.01	0.05±0.01
2-butanol	58.94±1.28	415.51±1.76	90.49±2.54	109.46±2.11	127.52±1.26	123.46±2.11	169.66±1.17
1-hexanol	ND	12.09±0.98	ND	ND	ND	ND	ND
2-phenylethanol	4.11±0.26	ND	ND	ND	ND	20.56±0.37	ND
Total higher alcohols	***325.29±5.42***	***2313.11±10.24***	***428.22±6.66***	***566.24±8.21***	***786.03±6.43***	***737.04±7.82***	***1017.31±6.68***
Ethyl acetate	42.22±2.10	112.82±1.93	83.93±1.47	91.54±1.59	53.17±0.96	73.55±0.59	91.22±3.12
Propyl acetate	0.05±0.01	ND	0.05±0.01	0.05±0.01	ND	0.05±0.01	ND
Isopropyl acetate	ND	0.05±0.01	0.05±0.01	ND	ND	ND	ND
Ethyl butyrate	ND	ND	0.05±0.01	ND	ND	0.05±0.01	ND
Ethyl caprylate	ND	ND	0.05±0.01	ND	ND	ND	ND
Phenyl acetate	3.29±0.16	17.89±0.28	ND	ND	ND	ND	0.05±0.01
Ethyl hexanoate	ND	0.05±0.11	0.05±0.01	ND	5.11±0.32	6.84±0.31	0.05±0.01
Ethyl decanoate	13.14±0.57	32.56±1.11	0.05±0.01	21.06±0.23	15.72±0.19	0.05±0.01	0.05±0.01
Total esters	***58.70±2.84***	***163.37±3.44***	***84.23±1.53***	***112.65±1.83***	***74.00±1.47***	***80.54±0.93***	***91.37±3.15***
α – terpineol	ND	0.05±0.01	ND	ND	0.05±0.01	ND	0.70±0.09
Nerol	ND	0.05±0.01	0.05±0.01	0.05±0.01	ND	ND	0.05±0.01
β – citronellol	0.05±0.01	0.37±0.06	0.05±0.01	ND	ND	0.05±0.01	0.05±0.01
Geraniol	0.05±0.01	0.05±0.01	0.05±0.01	0.05±0.01	0.05±0.01	0.05±0.01	0.20±0.04
Total terpenes	***0.10±0.02***	***0.52±0.09***	***0.15±0.03***	***0.10±0.02***	***0.10±0.02***	***0.10±0.02***	***1.00±0.15***
TOTAL CONTENT	***464.75±10.29***	***2854.84±18.78***	***654.70±10.42***	***851.14±12.90***	***1010.07±9.65***	***994.57±11.94***	***1355.41±11.59***

When 50% ethanol hawthorn berries extracts was used in variant 1000:20, a total terpene content was similar to that in the control. In variant 1000:80 terpenes have not been identified. All other variants shown a quantitative terpene composition (0.10 ± 0.02 mg/dm^3 - 0.56 ± 0.13 mg/dm^3) higher than the control one.

When 70% ethanol extracts of hawthorn berries was applied in absolutely all experimental variants, a total terpene content (0.10 ± 0.02 mg/dm^3 - 1.00 ± 0.15 mg/dm^3) was found to be significantly higher than that found in the control sample.

It is apparent that incorporation of hawthorn (flowers and berries) extracts into the distillate led to an increased and complicated terpene composition. The terpenes are compounds with reported biological activities, which reflect in improving of the aromatic composition and biological potential of these new distillates with added extracts from plant sources. It was noted that the incorporated hawthorn berries extracts led to higher final terpenes than the hawthorn flowers extracts experimental groups. The increased content of terpenes in the distillate is due to the terpene composition of the used plant source. The main terpene identified in all variants (where terpenes were found) was geraniol.

CONCLUSION

From the study on the aromatic characterization of distillates with added hawthorn flowers (*Crataegus monogyna - Rosaceae*) and hawthorn berries (*Crataegus monogyna - Fructus*) extracts, the following conclusions can be drawn:

● The incorporation of hawthorn flowers and berries extracts resulted in the quantitative growth of common volatile compounds in some of the experimental variants. The incorporation of 50% ethanol hawthorn flowers extracts shown the best prospect of increasing the total volatile composition when these extracts were incorporated into the distillate.

● The incorporation of 50% hawthorn flowers ethanol extracts resulted in significant quantitative growth of the higher alcohols fraction.

● The presence of four basic higher alcohols in all experimental variants was found: 3-methyl-1-butanol, 2-methyl-1-butanol, 1-propanol and 2-butanol. Of these, 3-methyl-1-butanol was characterized by the highest quantitative presence.

● One major aldehyde - acetaldehyde - has been identified. In all variants its amounts corresponded to the normal presence values in which it exerts a positive influence on the aromatic profile of the distillates.

● With regard to total ester content, the study proved that 50% ethanol hawthorn flowers and berries extracts were a better prospect for the complication of total ester composition than 70%. Ethyl acetate was the major ester identified practically in all the distillates studied.

● All established concentrations of methyl alcohol were in the range of its normal presence.

● The incorporation of hawthorn (flowers and berries) extracts led to an increased and complicated terpene composition of the distillates. This reflected in improved aromatic and biological potential.

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