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CHERRY DISTILLATES. PART II. CHEMICAL AND SENSORY ASSESSMENT OF DISTILLATES OBTAINED FROM FERMENTED CHERRIES

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Key words: cherry fruit, cherry distillate, gas chromatography, components of aroma.

A chemical and sensory assessment of cherry distillates was carried out. Essential differences were observed in the chemical composition of distillates obtained from mashes fermented with yeasts strain Cherry 8 and Burgund 39. The correlation was confirmed between the presence of crushed kernels and green parts in the mash and the content of hydrocyanic acid and hexyl alcohol in distillates.

The aroma components of fruit distillates derived from the raw material, from yeasts or which are produced during fermentation or distillation and maturation may bring about positive or negative sensory features affecting the quality of the final product.

The relevant literature quotes many components of aroma in alcohol beverages obtained by the natural fermentation method [1, 4, 9, 11, 15, 21, 23].

Together with the development of analytical methods, the aroma components of whisky [16, 17] of vodkas [10] and of fruit distilates [1, 3] are identified and quantitatively determined. The quantitative shares of the particular groups of compounds and of single components as well as their mutual ratio play a very important role the final aroma of distillates [1, 5, 16, 18, 22]. The typical components present in fruit distillates are: benzyl and hexyl alcohols, methanol, hydrocyanic acid and others [19, 20].

Various chemical compounds which are present in the composition of aroma of fruit distillates have wider or narrower limits for smell sensibility what has a substantial influence on the final effect or aroma [13, 14, 16].

The problems of the chemical composition of the aroma of fruit distillates are essential not only in terms of their cognitive aspects but also because of the existing possibilities for a correlation of their composition with the sensory evaluation and production technology.

An elaboration of such correlations would make it possible to control the process of fermentation, distillation and maturation aimed at obtaining, from the sensory viewpoint, the most desired composition of aroma in fruit distillates.

The purpose of this work was to make a chemical and sensory evaluation of cherry distillates with a definition — based on this above evaluation — of the components typical of these distillates.

MATERIALS AND METHODS

The experiments were carried out according to the description presented in the first part of this work. For fermentation of mash from juice cherries, yeasts of strain Cherry 8 and Burgund 39, were used. Additionally, the following factors were studied: influence of the quantity of crushed kernels on the content of hydrocyanic acid in spirits and in distillates, influence of adding green parts (leaves, pedicles) to mashes before fermentation on the level of hexyl alcohol and the influence of heat treatment of mashehs on the quantity of methanol produced.

In these cases defined quantities of fruit with the crushed kernels or with a weighed amount of green were added to the mashes prior to fermentation. The mashes destined for heat treatment were heated by membrane method to the determined temperature with a simultaneous constant movement of the agitator, they were kept for a present period of the time and cooled to room temperature for 10-15 minutes and then the yeast sediment was added and fermentation was carried on as in the case of other samples.

Cherry distillates obtained from mashes with yeasts Cherry 8 and Burgund 39 which proved to be the most suitable (part I of the present work) were the subject of further chemical and sensory studies.

An evaluation of distillates acc. to Micko [23] will be presented in the part II of this work.

Diacetyl was determined by Brenner's method [2], as modified by Rodopuło et al [12].

Acetals were determined by Rebelein method acc. to Misselhorn [6]. The chromatographic determinations were made in a chromatograph Pye Unicam 204.

The following packings of columns were applied:

— for fusel alcohols — triethanolamine with sodium capronate + Chromosorb W,

— for esters and fatty acids — Reoplex 400 + Chromosorb W,
— for aldehydes — didecyl phthalate + Chromosorb P;
— for alcohols: benzyl-, hexyl-, and β-phenoloethyl alcohols —
— modified Carbowax FFAP (2-nitroterephthalate of Carbowax 20 M) + + Chromosorb W/NAW, acc. to the method of Tuttas and Beye [20].

The sensory evaluation and other determinations were performed acc. to Polish Standards [7, 8].

RESULTS AND DISCUSSION

Table gives the characteristic of cherry distillates obtained from mashes fermented with yeasts strain Cherry 8 (distillate A) and strain Burgund 39 (distillate B). Distillates A in comparison to distillates were characterized, as a rule, by a higher level of total esters, by about 10.4% in the average, of fusel alcohols (by about 24%) and of diacetyl and hydrocyanic acid content. Such groups of compounds as volatile acids, volatile esters and aldehydes were present in larger amounts in distillates B.

A characteristic feature is the lower level of methanol in distillate A, by about 20% in the average and the considerably higher level of "total esters minus calculated esters" (Table, column 10) — 22.0 for distillate A and 8.35 for distillate B respectively.

Too low values of this difference (usually below 5.0) were mostly recorded in distillates with a sensible "acetic touch".

These results were confirmed by a sensory evaluation of distillates: "A" distillates received as a rule higher scores in the grading scale of evaluation.

Fig. 1a presents the characteristic features of distillates in terms of the level of fusel alcohols. Noteworthy is the relatively high level of 1-propanol and isobutanol. The calculated ratio of 1-propanol : isobutanol varied from 1.0 to 4.5, and in case of good distillates from the organoleptic viewpoint it amounted to 1.5-1.3.

These alcohols seem to be the specific components of cherry distillates.

Yeasts of Burgund strain — in comparison to yeasts of Cherry strain produced higher quantities of these two alcohols as well as of 1-butanol and lower quantities of amyl alcohols. 1-butanol was present in all distillates B while in distillates A, the presence of this compound was found only sporadically. Such alcochols as: benzyl-, hexyl- and β-phenyloethyl ones were found in all examined samples (Fig. 1b).

The concentrations of hexyl, and β-phenyloethyl alcohol were similar in distillates A and B, while benzyl alcohol was found in higher quantities in distillates B.

Table. Characteristics of distillates*)

Specification	Sensory assessment (points)	Concentration of ethanol (strength) % vol.	pH	Total acidity	Volatile acidity	Total esters	Volatile esters	Calculated total esters**
				mg/100 cm³ 100°				
Distillate A	4.5	71.6	4.95	8.5	0.44	55.4	8.4	33.4
	4.0	69.1	4.70	6.0	0.33	38.7	4.2	27.0
	5.0	72.7	5.30	12.0	0.67	73.6	12.2	43.5
Distillate B	4.0	73.1	5.15	10.6	0.95	47.5	14.0	39.15
	3.0	70.2	4.85	8.3	0.72	31.3	8.0	32.8
	4.5	76.2	5.55	15.0	1.20	65.0	20.5	51.2

*) The table lists the mean results, lowest and highest

**) This value was calculated using the following formula $E_{cal.} = 2.75\,S + 10$, S = total acidity estimated by colorimetric method.

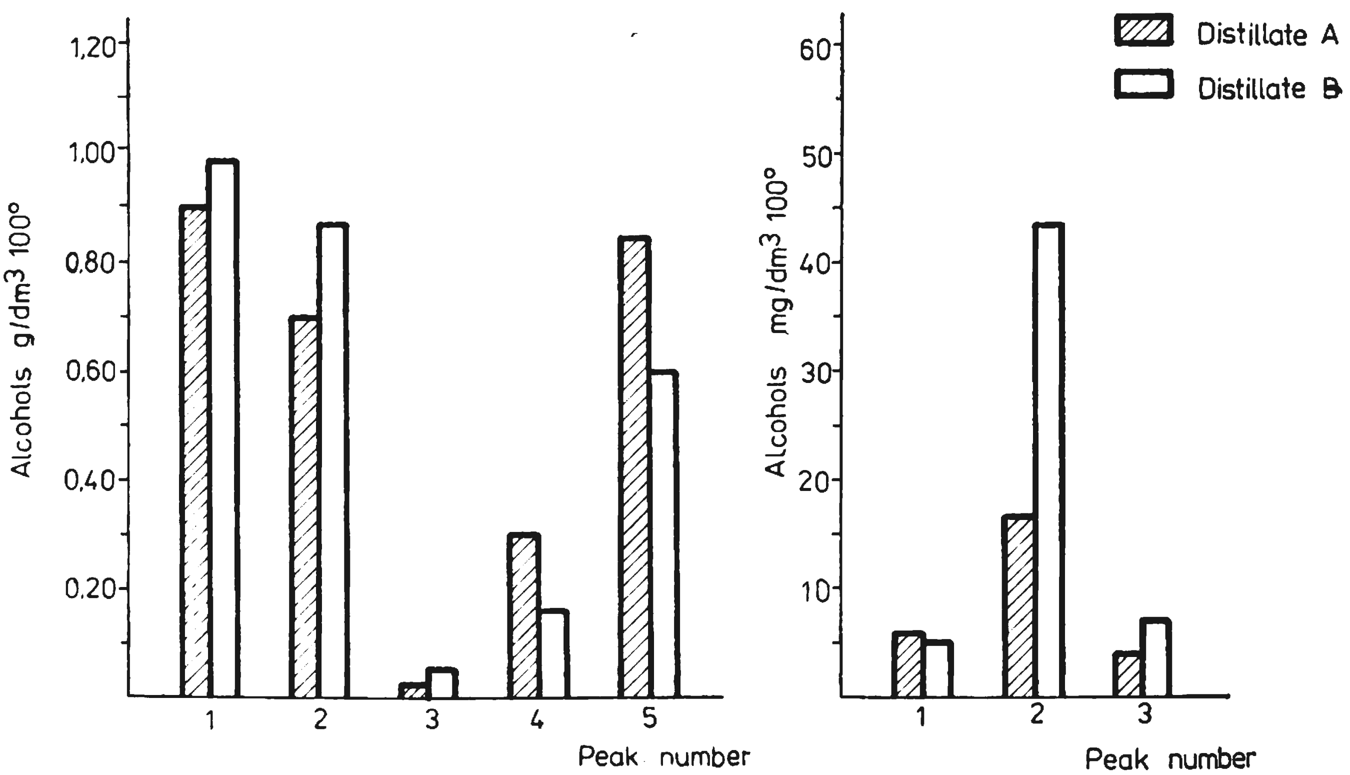

Fig. 1a. Fusel alcohols in cherry distillate: 1 — n-propyl alcohol, 2 — isobutyl alcohol, 3 — butyl alcohol, 4 — 2-methylobutanol-1, 5 — 3-methylobutanol-1

Fig. 1b. Alcohols-, benzyl-, hexyl-, and β-phenyletyl in distillate: 1 — hexyl alcohol, 2 — benzyl alcohol, 3 — β-phenyletyl alcohol

Fig. 2 illustrates the formation of hydrocyanic acid, methanol and hexanol content in crude spirits and distillates produced from mashes-fermented with yeasts of Burgund strain.

Hexyl alcohol is produced from linolenic acid which in turn derives mainly from the green parts of plants and of unripened.

The presence of this alcohol gives a bitter, stinging taste to the distil-

Total esters minus calculated esters	Aldehydes	Fusel alcohols	Methanol % vol.	Acetals	Furfural	Diacetyl	Hydrocyanic acid
	g/dm³ 100°			mg/dm³ 100°			
+22.0	0.055	3.1	0.35	20.2	12.5	2.0	5.5
+11.7	0.034	2.0	0.15	17.6	4.4	0.8	1.5
+30.1	0.070	3.8	0.45	22.0	17.0	4.0	17.0
+8.35	0.075	2.5	0.45	20.0	12.7	1.2	4.2
−1.5	0.050	1.0	0.25	16.0	3.7	0.5	2.5
+13.8	0.200	3.5	0.62	24.7	17.1	3.1	12.0

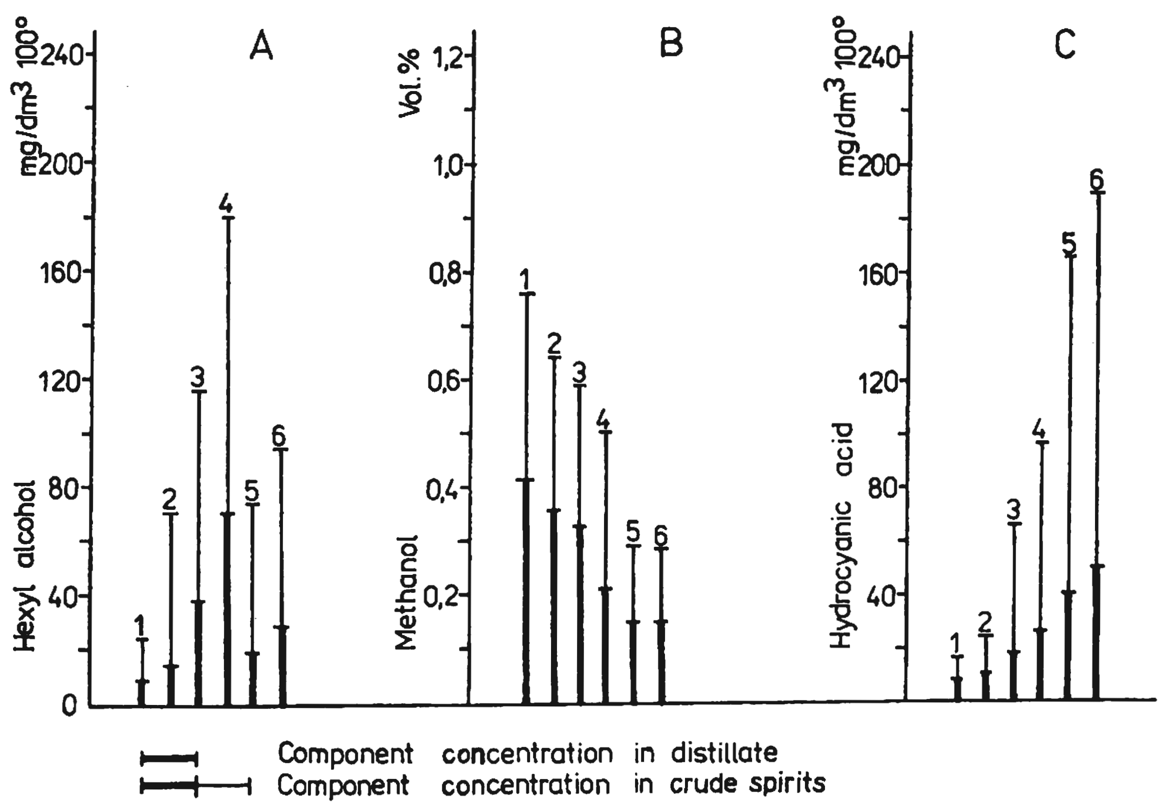

Fig. 2. Hydrocyanic acid, methanol and hexyl alcohol in crude spirits and distillates; A — hexyl alcohol, gm/dm³ 100°; 1 — control test — fruits at full maturity, 2 — fruits at full maturity + 1 g/kg green parts, 3 — fruits at full maturity + 3 g/kg green parts, 4 — fruits at full maturity + 6 g/kg green parts, 5 — fruits at full maturity + 50 g/kg green parts, 6 — fruits at full maturity + 100 g/kg green parts; B — methanol, % vol.; 1 — control test — mash without heat treatment, 2 — thermal treatment — 65°C, 30 min, 3 — thermal treatment — 85°C, 15 min, 4 — thermal treatment — 85°C, 30 min, 5 — thermal treatment — 95°C, 10 min, 6 — thermal treatment — 95°C, 20 min; C — hydrocyanic acid, mg/dm³ 100°; 1 — control test — fruits without kernels, 2 — whole fruits, 3 — 10% wt. of fruits with crushed kernels, 4 — 25% wt. of fruits with crushed kenels, 5 — 50% wt. of fruits with crushed kernels, 6 — 75% wt. of fruits with crushed kernels

late and for this reason its presence in the final product is not desirable.

The level of hexyl alcohol (Fig. 2a) in crude spirits varied within) 20-180 mg/dm³ 100°, and in distillates 2-70 mg/dm³ 100°. The addition of 6 g green parts for 1 kg of fermented fruit caused a 5-fold increase of hexanol content in crude spirit. A similar influence to that of leaves and pedicles was exerted by green and unripened fruits — in this case, however, the increase of hexanol content was considerably smaller (Fig. 2a, peak 5 and 6).

The amount of hexyl alcohol separated during corrective distillation depended on its initial level in crude spirit used for distillation and it decreased together with the rise of concentration of this alcohol in the initial sample. In the average during the corrective treatment more than 50% of this alcohol was separated (in two trals even 85%).

Heat treatment of cherry pulp before fermentation did not bring the expected results (Fig. 2b). The distillates obtained from these trials were characterized by a lower level of methanol only from 10 to 60%. It should be assumed that, not only fruit pectin esterases participate in the pectin degradation, but also enzymes of this type present in yeast cells. The results show that the heat treatment of cherry mashes at 65°C and 85°C gives similar effects, while heating at 95°C allows to decrease the quantity of the methanol produced by about 60-80%.

All distillates obtained from mashes after heat treatment were characterized, in a sensory evaluation, by a smaller specifity of flavour and in the chemical assessment — by a lower level of esters and higher content of fusels and of furfural.

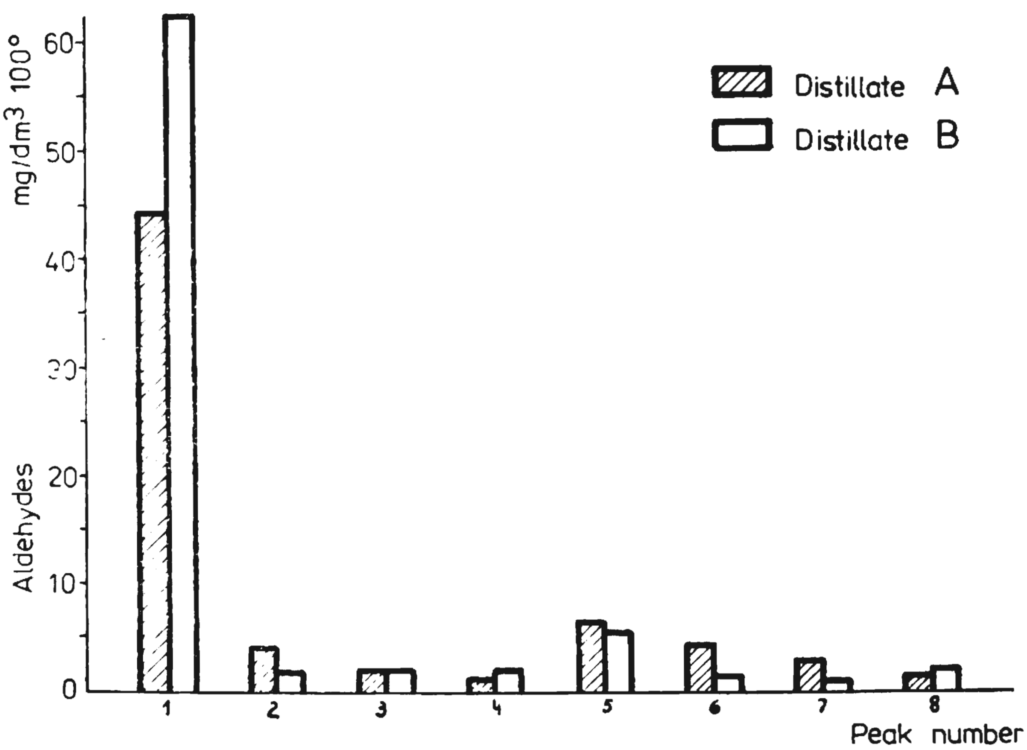

Fig. 3. Qualitative and quantitative composition of carbonyl compounds in cherry distillate: 1 — acetaldehyde, 2 — propionaldehyde, 3 — isobutyraldehyde, 4 — butyraldehyde, 5 — isovaleraldehyde, 6 — valeraldehyde, 7 — caproicaldehyde, 8 — unknown

As shown by the diagram (Fig. 2b) during corrective distillation, a large part of methanol passes to the head (first running) and tail fractions, in the average from 30 to 65% of its initial quantity in crude spirit.

Fig. 2c illustrates the influence of the quantity of crushed kernels in the fermented mash on the hydrocyanic acid level in crude apirit and distillate. The increase of hydrocyanic acid level was not directly proportional to the quantity of crushed kernels.

Crude spirits deriving from the distillation of fermented mashes which were prepared from whole or drilled fruits contained 15-22 mg hydrocyanic acid in 1 dm^3 100° alcohol, but when there were 10% crushed kernels present, the amount of HCN was increased by 40-70 mg/dm^3 100° and 50% presence of such kernels in the mash gave 120-170 mg/HCN/dm^3 100° alcohol. The presence of hydrocyanic acid in spirits and distillates obtained from drilled and whole fruits may be explained by the probable diffusion of cyanic compounds from the kernels to the fruit pulp both during the ripening period and during the fermentation process. Most typical in terms of taste, cherry distillates contained hydrocyanic acid in the quantities ranging from 2 to 20 mg/dm^3 100°. After corrective distillation of spirits, the level of hydrocyanic acid in distillates was lowered 2-5 times in comparison to its content in crude spirits. The qualitative and quantitative composition of aldehydes in the distillates examined (Fig. 3) re-

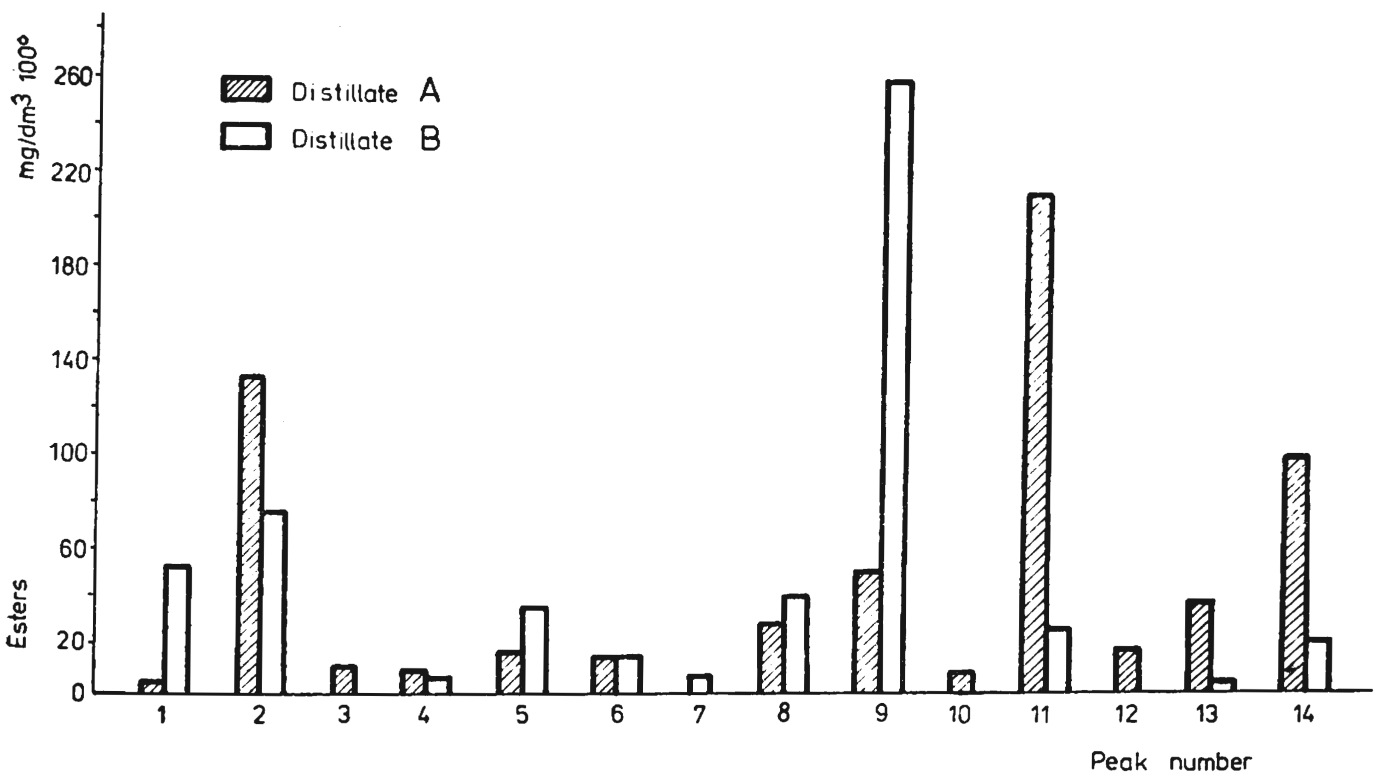

Fig. 4. Qualitative and quantitative composition of esters in cherry distillates; 1 — methyl propionate + ethyl isobutyrate, 2 — ethyl acetate, 3 — ethyl propionate, 4 — methyl butyrate, 5 — isobutyl acetate, 6 — ethyl butyrate, 7 — amyl formate, 8 — isobutyl propionate + n-butyl acetate, 9 — isoamyl acetate + ethyl valerate + isopropyl valerate, 10 — amyl acetate, 11 — isoamyl propionate, 12 — unknown, 13 — unknown, 14 — ethyl laurate

veals their small differentiation depending on the applied strain of yeats. Acetic aldehyde is the predominating compound; it constitutes about 80% of the total quantity of aldehydes.

The qualitative and quantitative compositions of esters (Fig. 4) are more differentiated. In most of the distillates examined the following esters were present in comparatively big quantities ethyl acetate (peak 2), sum of isoamyl acetate+ethyl valerate and isopropyl valerate (peak 9), and isoamyl propionate (peak 11) and ethyl laurate (peak 14). A characteristic feature is the absence of ethyl propionate, n-amyl acetate and of an unidentified compound (peak 12) in distillates B.

For a more complete interpretation of the results, the following indices were calculated for the distillates examined: esters minus ethyl acetate and esters minus ethyl acetate/esters ×100. Values of difference "esters minus ethyl acetate" varied from 200 to 600 mg/dm³ 100° and in a correlation with the organoleptic evaluation of these distillates, the result 200-300 mg/dm³ 100° should be considered as a good index. In case of both greater and smaller differences, the score evaluations of distillates were lower. The second index accepted values within the limits of 20-100. According to Bandion [1] for good fruit distillates and cognacs, this index amounts from 20 to 60 and its lowering to the lowest values may be a proof of acetic touch. On the basis of an examination of cherry distillates, the value 20-50 should be accepted as a good index. The more abundant composition of esters of higher fatty acids in distillates A, in comparison to distillates B with a simultaneous higher level of ethyl

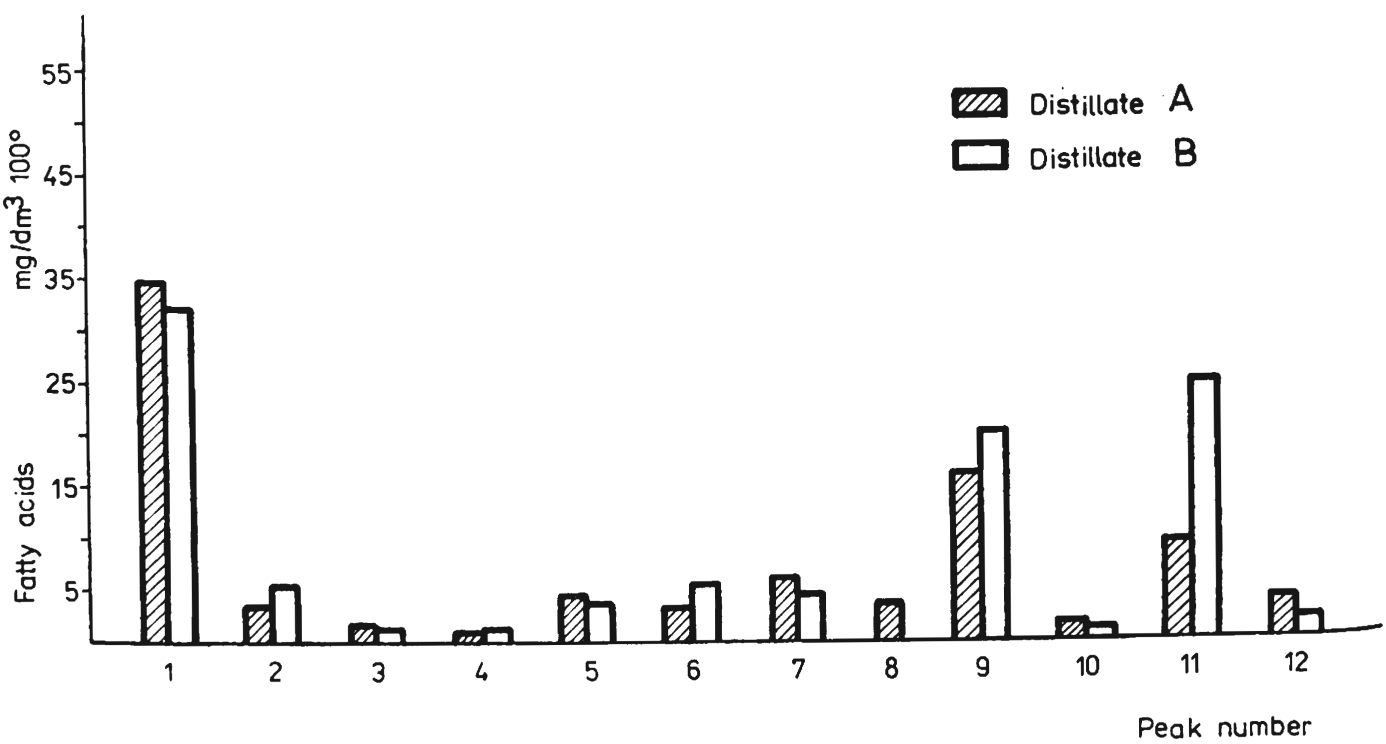

Fig. 5. Qualitative and quantitative composition of fatty acids in cherry distillates; 1 — acetic acid, 2 — propionic acid, 3 — isobutyric acid, 4 — butyric acid, 5 — isovaleric acid, 6 — valeric acid, 7 — hexanoic acid, 8 — enanthic acid, 9 — caprylic acid, 10 — pelargonic acid, 11 — unknown, 12 — unknown

acetate makes it possible to assume that the essential factor in the formation of sensory properties is the proper ratio of ethyl acetate and esters of higher fatty acids.

In the group of fatty acids (Fig. 5), the main position in terms of quantity belonged to acetic acid which constituted 20-60% of the total amount of acids present in the distillates examined.

The following other acids were found: propionic, isobutyric, butyric, isovaleric, caproic, enanthic, caprylic and pelargonic. On the chromatograms of acids the presence of two unidentified compounds was found (peaks 11 and 12) and component no 11 were usually found in considerable quantities, especially in distillates B. The presence of enenthic acid (peak 8) was also characteristic; this compound was noted in all distillates A but was not identified in distillates B.

CONCLUSIONS

1. The typical components of cherry distillates are e.g. 1-propanol and isobutanol, benzyl alcohol, isoamyl propionate and ethyl laurynate.

2. Cherry distillates obtained from mashes fermented with yeasts strain Burgund 39, in comparison to distillates obtained from mashes fermented with yeasts strain Cherry 8, are poorer from the quantitative and qualitative viewpoint in components accompanying ethanol, mainly in components belonging to the group of fatty acids and esters. A characteristic feature is the absence in these distillates of enanthic acid, ethyl propionate and n-amyl acetate.

3. The presence of hydrocyanic acid in cherry spirits is not directly proportional to the amount of crushed kernels in the fermented mash. Destruction of 50% kernels causes an increase of hydrocyanic acid level in spirit to about 160 mg/dm^3 100°. During corrective distillation, the quantity of hydrocyanic acid is lowered 2-5 times in comparison to its initial level.

4. The presence of green parts in the fermented mash has an influence on the production of higher quantities of hexyl alcohol. The addition of 1-6 g green parts for 1 kg of fermented mash of fruit causes an increase in the content of hexanol in spirit within 90-180 mg/dm^3 100°. During the corrective distillation of crude spirit, the content of this compound is lowered by more than 50% of its initial level.

5. The heat treatment of cherry pulp before fermentation decreases the quantity of produced methanol within 10 to 80%. The most favourable effects in this respect were obtained in a temperature of 95°C for 10 minutes.

During the corrective distillation of cherry spirits, the amount of methanol may be reduced by about 30-65% of its initial content.

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DESTYLATY Z WIŚNI. CZ. II. OCENA CHEMICZNA I SENSORYCZNA DESTYLATÓW OTRZYMYWANYCH Z PRZEFERMENTOWANYCH WIŚNI

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S t r e s z c z e n i e

Poddano ocenie chemicznej i sensorycznej destylaty wiśniowe otrzymane z zacierów przefermentowanych z drożdży rasy Wiśnia 8 i Burgund 39. Stwierdzono, że destylaty wiśniowe otrzymane z udziałem drożdży rasy Burgund 39 są uboższe w kom-

ponenty aromatu, głównie z grupy kwasów tłuszczowych i estrów oraz charakteryzują się mniejszą oryginalnością w ocenie sensorycznej (tab. 1, rys. 4 i 5). Za charakterystyczne składniki destylatów wiśniowych uznano: propanol-1, izobutanol, alkohol benzylowy oraz propionian izoamylu i laurynian etylu. Wprowadzenie do zacieru przed fermentacją 50% wag. rozmiażdżonych pestek powoduje wzrost ilości cyjanowodoru w spirytusie surowym do ok. 160 mg/dm^3 100° (rys. 2c).

Stwierdzono również, że dodatek od 1 do 6 części zielonych na kilogram fermentowanych owoców powoduje wzrost zawartości alkoholu heksylowego w spirytusie od 90-180 mg/dm^3 100° (rys. 2a). Zastosowanie obróbki termicznej do zacierów wiśniowych przed fermentacją pozwala obniżyć ilość tworzonego metanolu o ok. 60 do 80%. Najkorzystniejsze wyniki uzyskiwano, gdy stosowano temperaturę 95°C, w czasie 10 min (rys. 2b). Destylacja korekcyjna spirytusów wiśniowych pozwala na znaczne obniżenie zawartości cyjanowodoru (2- do 5-krotne), alkoholu heksylowego (ok. 50%) oraz metanolu (ok. 30 do 65%) w destylatach (rys. 2).