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CHEMICAL AND SENSORY ASSESSMENT OF FERMENTED PEAR DISTILLATES

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Key words: pear distillates, aroma components.

The physico-chemical and sensory characteristics of distillates of fermented mashes from "Bera Williams" pears were investigated. It was found that the distillates with untypical sensory characteristics contain a particularly high amount of hexyl alcohol, fusel alcohols and that they have a less varied qualitative and quantitative composition of esters and fatty acids.

The chemical and sensory properties of natural distillates depend on the kind and quality of the basic raw material, on the strain of yeasts used in the fermentation as well as on the methods of fermentation, distillation and maturation. The processes of fermentation and distillation are particularly important among those factors in view of the variety of transformations that accompany them. These transformations determine sented by the quoted authors indicate the considerable importance of n-propanol as a taste component. This constituent may be regarded as typical for distillates from Williams pears.

The problems of pear distillates quality were examined by, among others, Kain and Bandion [5], Nosko [9], Pieper [13] and Wucherpfennig and Bretthauer [25]. The chromatographic studies of such distillates presented by the quoted authors indicate the considerable importance of n-propanol as a taste component. This constituent may be regarded as typical for distillates from Williams pears.

The aim of the present research was a tentative chemical and sensory characteristic of pear distillates and, if possible, the indication of the chemical components responsible for the poor quality of the distillates reflected in their low position on the quality point scale.

MATERIAL AND METHODS

The research material consisted of four distillates produced in industrial conditions and six distillates obtained in the laboratory. Five samples were selected for the purpose of results presentation; two of them were industrial distillates (A and B) and the other three were produced in the laboratory (C, D and E). The distillates were produced from pears of the Bera Williams autumn variety grown in south-eastern Poland, ripe for consumption (laboratory samples) or of varying maturity (industrial distillates). Disintegrated fruit were fermented with 5% vol. pure culture of Syrena yeast concentrate obtained from the Collection of Pure Cultures of Łódź Technical University. The size of individual laboratory samples ranged from 5 to 7 kg. The industrial samples were fermented with a 2% addition of a concentrate of the same yeast strain. The separate samples fermented for 20-24 days at 18-25°C. The fermented mashes were distilled in suitable laboratory or industrial copper apparatus with indirect heating. The obtained crude spirits with 15-20% vol. alcohol content were distilled once more (corrective, fractional distillation) and this process yielded 2% vol. of heads, 88% of the fraction proper (distillate) and about 10% of the tail fraction (calculated as 100% alcohol). The fractional distillation of laboratory samples was performed with a copper-glass apparatus with a water jacket in which the distillation pot, column and head were copper while the cooler and collector, the calibrated tank and the receiver were made of glass. The column of the apparatus, 110 cm high and 11 cm in diameter, was filled with ceramic Raschig rings up to the height of 70 cm. The corrective distillation of industrial samples was done in the same copper apparatus in which the fermented mashes were distilled. The distillates thus obtained were the object of further studies.

The basic physico-chemical and sensory determinations were done with standard methods [14, 15]. Acetals were determined with Rabelein's method according to Misselhorn [8], and diacetyl by Brenner's method [3] as modified by Rodopuło et al. [17]. Also assessed was the odour yield from the direct sample and after its fractionation [25]. Chemical compounds from the group of esters, alcohols and fatty acids were identified chromatographically and their quantities were determined. The chromatographic analyses were done in a Pye Unicam 204 apparatus with a flame-ionization detector and a numerical integrator.

Fusel alcohols and methanol were determined in the direct sample: column length 2.1 m, diameter — 4 mm; Chromosorb W 60/80 mesh + + triethanolamine + 1% sodium caproate, Chromosorb-to-liquid phase rati 87.5 : 10, column temperature 85°C, detector and doser temperature 130°C carrier gas — nitrogen 40 cm^3/min.

Determination of benzyl and hexyl alcohols: preparation of sample for

analysis according to Tuttas and Beye [23]; column length 3 m, diameter — 4 mm; Chromosorb W NAW 60/80 mesh+10% weight FFAP modified Carbowax (2-nitroterepthalate of Carbowax 20M), column temperature programmed from 50 to 170°C with temperature increment rate 6°C/min, detector temperature 220°C, doser temperature 250°C, carrier gas — nitrogen 40 cm^3/min.

The determination of esters consisted in their extraction from the distillate with n-pentane and in chromatographic analysis of the concentrated extract: column length 2 m, diameter — 4 mm; Chromosorb W 60/80 mesh+10% weight Reoplex 400, column temperature 65°C, detector and doser temperature 125°C, carrier gas — nitrogen 60 cm^3/min.

The method of determining fatty acids involved measurements of the quantitative emission of sodium salts of these acids from the distillate and the liberation of free fatty acids with an orthophosphoric acid solution in acetone directly prior to chromatographic analysis: column length 2 m, diameter — 4 mm; Chromosorb W 60/80 mesh+10% weight Reoplex 400, column temperature 160°C, detector temperature 220°C, doser temperature 250°C, carrier gas — nitrogen 60 cm^3/min.

RESULTS AND DISCUSSION

The extensiveness of the performed chemical and sensory evaluation of the studied distillates makes it impossible to give a full presentation of the obtained results. Among others we omit the detailed assessment of samples after their fractionation.

The diagrams present a chemical characteristic of two distillates and pertain to samples which received the minimum (distillate A) and the maximum (distillate E) number of points in the sensory assessment. The chromatographic characteristics of the other studied samples as regards most of the components were similar to the chemical composition of distillate A or E.

Table 1 presents the general chemical and sensory characteristic of the studied pear distillates. The total acids and volatile acids contents were fairly diversified in the individual samples, this being especially true of the latter: that ranged from 0.96 to 9.17 mg/100 cm^3 of pure alcohol distillate.

The total esters content ranged from 22.4 (sample A) to 45.8 mg in sample E and 56.1 mg/100 cm^3 of pure alcohol distillate in sample B.

The sum content of fusel alcohols in the investigated distillates must also be regarded as considerably varied. Samples C. D and E had 1.0-1.52 g of these alcohols per dm^3 of pure spirit distillate, while in samples A and B their content was visibly higher (2.05 and 3.15 g/dm^3 100%).

Table 1. Chemical and sensory characteristic of pear distillates

Specification	Sample				
	A	B	C	D	E
Alcohol content (% vol)	70.5	76.0	68.5	70.5	71.2
Total acidity*) (mg/100 cm³ of 100% spirit)	6.30	16.10	4.55	5.00	6.82
Volatile acidity (mg/100 cm³ of 100% spirit)	3.05	9.17	0.96	2.48	2.10
Total esters**) (mg/100 cm³ of 100% spirit)	22.40	56.10	31.00	28.10	45.80
Fusel alcohols***) (g/dm³ of 100% spirit)	2.05	3.15	1.00	2.10	1.52
Aldehydes (mg/100 cm³ of 100% spirit)	19.52	7.20	6.00	9.80	7.55
Acetals (mg/100 cm³ of 100% spirit)	1.32	1.20	2.20	2.20	1.54
Methanol (mg/100 cm³ of 100% spirit)	270.07	378.12	182.00	222.10	243.00
Diacetyl (mg/dm³ of 100% spirit)	0.30	0.90	1.11	0.72	0.25
Furfural (mg/dm³ of 100% spirit)	5.10	20.00	7.01	6.00	5.15
pH	5.55	6.00	5.20	4.95	5.05
Sensory assessment (points)	2.5	3.0	4.5	3.0	5.0
Odour yield from direct sample	1:100	1:250	1:850	1:350	1:1000
Odour yield according to Micko	1:800	1:1200	1:3500	1:1500	1:3500

*) as acetic acid, **) as ethyl acetate, ***) as isoamyl alcohol

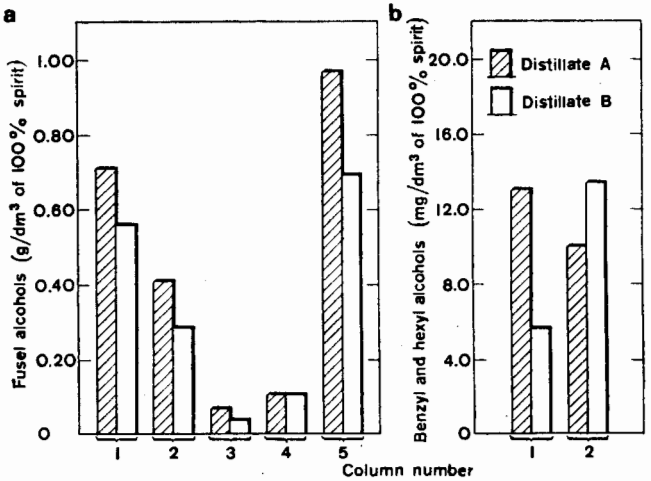

Fig. 1. a. Fusel alcohols in pear distillates; 1 — 1-propanol, 2 — 2-methylpropanol-1 (2MP-1), 3 — 1-butanol, 4 — 2-methylbutanol-1 (2MB-1), 5 — 3-methylbutanol-1 (3MB-1). b. Benzyl and hexyl alcohols in pear distillates; 1 — hexyl alcohol, 2 — benzyl alcohol

The quantities of acetals and aldehydes also differed significantly in the separate distillates. The greatest amounts of acetals were found in samples C and D (over 2.0 mg/100 cm^3 of pure alcohol distillate); the figures in the remaining distillates were lower. The aldehydes content was relatively least varied, with the exception of distillate A which showed an aldehyde content of more than 19 mg/100 cm^3 of pure spirit distillate.

The sensory evaluation revealed that distillates A and B differed considerably as regards taste and odour characteristics from the remaining samples. An exception in this respect was distillate D which equalled sample B on the evaluation point scale. The odour yield in the direct material as well as after this material's fractionation was much higher in distillates obtained in the laboratory (Table 1). Distillates C and E in particular were characterized by a clearly detectable original odour of the basic raw material. Samples A, B and D were markedly less typical as regards odour and taste, both at the stage of direct material and after its fractionation, and were marked by the so called acetic whiff detectable in the odour. Distillates A and B had a particularly intense odour of the light fractions, and their taste was poorly harmonized and burning. It seems that some of these negative features, and especially the reduced originality (authenticity of sensory properties of the basic raw material) and the burning taste, are a consequence of the considerable fusel alcohols content which in samples A and B was about 100% higher than in the other studied distillates.

Table 2. Chemical characteristic of pear distillates — calculated indices

Specification	Sample				
	A	B	C	D	E
Calculated esters*) (mg/100 cm^3 of 100% spirit)	27.32	54.27	22.51	23.75	28.75
Total esters minus calculated esters (mg/100 cm^3 of 100% spirit)	—4.92	+1.83	+8.49	+4.35	+17.05
Total esters minus ethyl acetate (mg/dm^3 of 100% spirit)	119.5	110.8	296.5	148.8	260.0
$\frac{\text{Esters} - \text{ethyl acetate}}{\text{esters}} \times 100$	49.8	19.8	85.5	52.3	144.4
P- 1/2MP- 1	1.75	1.80	2.25	1.92	1.96
2MB- 1+3MB- 1 (g/dm^3 of 100% spirit)	1.06	0.82	0.25	0.38	0.78

*) — esters calculated from the formula $E = 2.75 \times S + 10$, where S is the total acid content
P- 1 — n-propyl alcohol
2MP- 1 — 2-methylpropanol-1
2MB- 1 — 2-methylbutanol-1
3MB- 1 — 3-methylbutanol-1

Fig. 1 presents the quantitative and qualitative characteristic of the studied samples as regards fusel alcohols content. As can be seen in the diagram, distillate A contained clearly higher quantities of the determined alcohols than distillate E. Particularly characteristic in the former is the higher content of propanol which came to be regarded as a typical element of this type of product from Williams pears [12, 13, 24]. It is believed that increased contents of propanol have no adverse effect on the quality of cognac-type vodkas and distillates. On the other hand, in distillate E there is about 50% less butyl alcohol than in distillate A (Fig. 1, column 3). The total content of amyl alcohols (2MB-1 and 3MB-1) ranged from 0.25 to 1.06 g/dm^3 of pure spirit distillate (Table 2). It sppears that the mutual proportions between the various fusel alcohols are more important for the quality of distillates than their total content. The quantitative proportion between propyl and amyl alcohols is particularly significant. A large amount of amyl alcohols lends the distillates an unplesant taste which may be described as „moonshine" flavour. Propyl alcohol on the other hand has no such unfavourable effect on the sensory quality of distillates [4].

The characteristic of the studied samples as regards the content of hexly (AH) and benzyl (AB) alcohols is given in Fig. 1 together with data for fusel alcohols. The distillate lowest on the point scale (sample A) contained 13 mg AH/dm^3 of pure alcohol distillate, while in sample E the respective figure was 5.8 mg. Tanner [20, 21] claims that already 1 mg AH in 1 dm^3 of beverage causes a clear change of taste, producing a flavour of wood. Hexyl alcohol is a product of linolenic acid transformation during enzymatic oxidation. Linolenic acid is present in green parts of plants as well as in unripe fruits [21].

The amounts of benzyl alcohol found in the studied distillates ranged from 2.0 to 14 mg/dm^3 of pure spirit distillate. As can be seen in the presented diagram (Fig. 1) sample E contained over 6 mg benzyl alcohol more than sample A. This component, however, may be regarded as typical for kernel fruit distillates.

Fig. 2 presents the quantitative and qualitative characteristic of esters in the investigated samples. The qualitative composition of esters was similar in all the evaluated distillates but the samples with positive sensory features exhibited a more varied quantitative esters composition. Ethyl acetate was of course dominant, and its content in distillate E was much higher than in distillate A. According to Pfenniger [11] and Reinhard [16] ethyl acetate has a decidedly negative effect on the odour yield of alcoholic beverages. The harmful role of this component consists primarily in reducing the role of the other esters since, when present in large quantities, it clearly dominates in the odour. It is precisely ethyl acetate and not acetic acid which is responsible for the so called acetic whiff perceptible in the sensory evaluation of alcoholic beverages. The

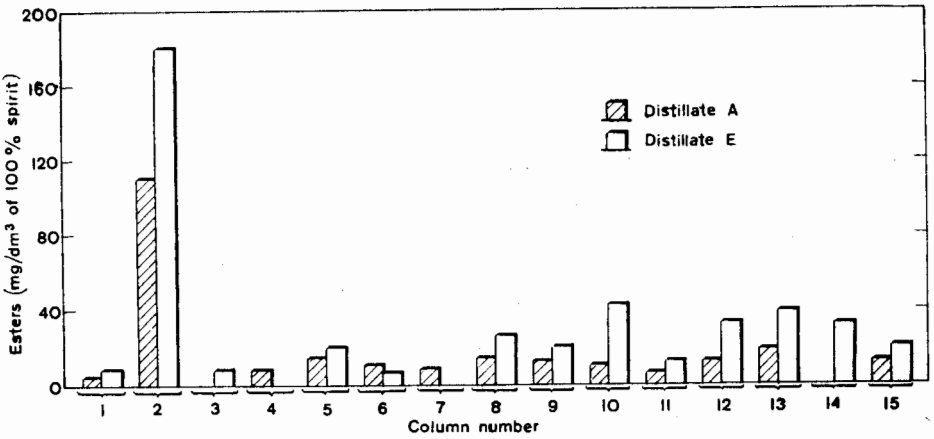

Fig. 2. Qualitative and quantitative characteristic of esters in pear distillates; 1 — methyl propionate+ethyl isobutyrate, 2 — ethyl acetate, 3 — ethyl propionate, 4 — methyl butyrate, 5 — isobutyl acetate, 6 — ethyl butyrate, 7 — amyl formate, 8 — isobutyl propionate+n-butyl acetate, 9 — isoamyl acetate, 10 — ethyl valerate+isopropyl valerate, 11 — n-amyl acetate, 12 — isoamyl propionate, 13 — unidentified, 14 — undentified, 15 — ethyl laurate

ethyl acetate content in sample E, higher by about 35% than in sample A, does not induce negative sensory properties in the distillate. It must be noted however that the total esters content in sample E is twice higher than in distillate A.

The characteristic quantities presented in Table 2 may suggest certain generalizations of the obtained results and are thus helpful in evaluations of fruit distillates. The amount of esters calculated according to Bandion's formula [1, 2] should in good-quality distillates be lower than the total esters content (Tables 1 and 2). In our study this rule failed to be confirmed only in distillate A (Table 2). In good fruit distillates and cognacs the index "total esters minus ethyl acetate" (Table 2) ought to range from 200 to 300 mg/dm³ of pure spirit distillate. This condition is satisfied only by distillates C and E in which this difference was 296.5 and 260 mg, respectively.

The other index, "esters minus ethyl acetate/esters×100", presented in Table 2 also took widely divergent values ranging from 19.8 in distillate B to 144.4 in sample E. It may be assumed that for good-quality distillates this value should be in the range 20-80 [1, 2]. However, the sensory evaluations of the studied samples did not confirm this rule, especially with regard to distillates A and E. This is probably due to the exceptionally low ethyl acetate content in some of the studied samples: a moderate amount of this ester, compared to the others may even lead to a milder taste of the distillate [6]. The presence in the studied samples of isobutyl and isoamyl esters called "fruit esters" by Suomalainen and

Nykänen [19], and of amyl acetate characterized by a pear odour [7] is particularly advantageous.

Foremost in the group of fatty acids, as regards quantity, is acetic acid, although considerable quantities of caprylic and lauric acids have also been found. Distillate E was characterized by a low acetic acid content and by a relatively voluminous quantity of an unidentified compound (Fig. 3, column 11), probably myristic acid. According to Nykänen et al. [10] acids such as the palmitic, the myristic, the enanthic and the palmitic-oleic positively affect the sensory properties of distillates. Enanthic acid was identified in sample E (about 2.5 mg/dm³ of pure alcohol distillate), but was not found in sample A.

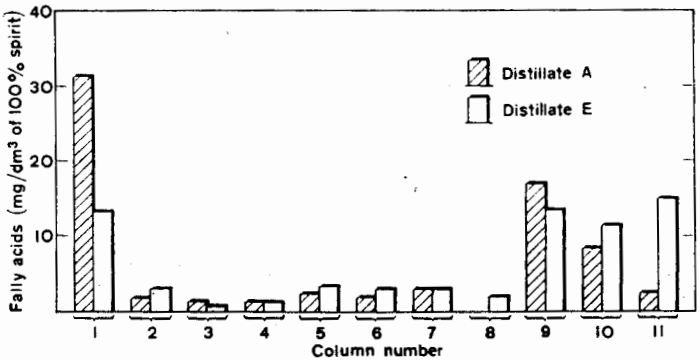

Fig. 3. Qualitative and quantitative characteristic of fatty acids in pear distillates; 1 — acetic acid, 2 — propionic acid, 3 — isobutyric acid, 4 — butyric acid, 5 — isovaleric acid, 6 — valeric acid, 7 — capronic acid, 8 — enanthic acid, 9 — caprylic acid, 10 — lauric acid, 11 — undentified

It may be surmised that among the factors responsible for the inferiour quality of distillate A as compared to distillate E were the following: (i) an about 25% higher fusel alcohols content, (ii) an about 50% higher content of hexyl alcohol, (iii) a poorer quantitative and qualitative composition of fatty acids and of these acids' esters. Despite the fact that sample E contained more ethyl acetate than sample A, its more varied esters composition and lower content of acetic acid probably caused the reduction of its so called sharpness.

CONCLUSIONS

1. Positive sensory properties were exhibited by the Williams pear distillates which had a more varied quantitative and qualitative composition of fatty acids and of esters thereof, and which contain small quantities of fusel alcohols (below 2 g/dm³ of pure spirit distillate) and less than 6 mg of hexly alcohol in 1 dm³ of pure spirit distillate.

2. The small sensory originality and the resultant low position on the sensory evaluation point scale may be due to the following factors:

— excessive hexyl alcohol content,

— relatively low total esters content compored to ethyl acetate presence,

— inadequate amounts of isoamyl acetate, amyl acetate, isoamyl propionate, and of ethyl valerate with isopropyl valerate,

— the absence of enanthic acid among fatty acids.

3. Calculated indices such as "total esters minus calculated esters" and "total esters minus ethyl acetate" are helpful in the evaluation of pear distillates. Positive values of the former, especially in excess of 5.0, indicate the preservation of advantageous proportions between acids and esters in the distillates. The value of the latter index in good-quality pear distillates should exceed 250 mg/dm^3 of pure spirit distillate.

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LITERATURE

1. Bandion F.: Mitt. Klosterneuburg 1972, **22** (3), 185.
2. Bandion F.: Mitt. Klosterneuburg 1972, **22** (4), 253.
3. Brenner M. W. and others: European Bevery Convention Procedings of the Congress, Bruksela 1963, **242**.
4. Cieślak J.: Przem. Ferment., 1961, 5 (8), 169.
5. Kain W., Bandion F.: Mitt. Klosterneuburg 1970, **20**, 375.
6. Klaushofer H., Bandion F.: Mitt. Klosterneuburg 1968, **18**, 359.
7. Krauze S.: Zarys nauki o środkach żywności, PZWL, Warszawa 1975.
8. Misselhorn K.: Die Branntweinw., 1963, **103** (14), 401.
9. Nosko S.: Die Kleinbrennerei 1974, **26**, 21.
10. Nykänen L., Puputti E., Soumalainen H.: J. of Food Sci., 1968, **33**, 88.
11. Pfenniger H.: Z. Lebensmittel Untersuch. und Forschung 1963, **156**, 401.
12. Pieper H. J.: Die Kleinbrennerei 1972, **24** (6), 49.
13. Pieper H. J.: Die Kleinbrennerei 1972, **24** (4), 32.
14. Polska Norma: PN-71/A-79528.
15. Polska Norma: PN-73/A-79529.
16. Reinhard C.: Dt. Lebensmitt. Rundsch., 1969, **65** (8), 224.
17. Rodopulo A. K., Kormakowa T. A., Pisarnickij A. E.: Vinod. Vinogr., 1971, **31** (7), 14.
18. Suomalainen H., Nykänen L.: Die Branntweinw., 1974, 114, 125.
19. Suomalainen H., Nykänen L.: Reprint from "Neeringsmiddelindustrien" 1970 (1-2), 1.
20. Tanner H.: Die Kleinbrennerei 1972, **24** (3), 19.
21. Tanner H.: Die Kleinbrennerei 1972, **24** (4), 29.
22. Tanner H., Brunner H. R.: Obstbrennerei heute, Heller Chemie und Verwaltungsgesellschaft mbH, Schwäbisch Hall 1982, 62.
23. Tuttas R., Beye Fr.: Z. Lebensmitt. Untersuch. und Forschung 1974, **167** (2), 88.
24. Wucherpfennig K., Bretthauer G.: Alkohol Ind., 1974, **87** (3), 43.

25. Wucherpfennig K., Bretthauer G.: Alkohol Ind., 1974, 87 (1), 7.
26. Wüstenfeld H., Haeseler G.: Trinkbranntweine und Liköre, Paul Parey, Berlin 1964, 400.

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OCENA CHEMICZNO-SENSORYCZNA DESTYLATÓW Z PRZEFERMENTOWANYCH GRUSZEK

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Streszczenie

Poddawano fizykochemicznej i sensorycznej charakterystyce destylaty z przefermentowanych gruszek odmiany Bera Williamsa. Przeprowadzono identyfikację chromatograficzną oraz określono ilościowo związki chemiczne z grupy estrów, alkoholi oraz kwasów tłuszczowych. Stwierdzono, że destylaty mające bardziej urozmaicony skład ilościowy i jakościowy wyższych kwasów tłuszczowych oraz estrów tych kwasów, a jednocześnie zawierające mniej alkoholi fuzlowych i heksanolu w stosunku do pozostałych badanych prób charakteryzują się pozytywnymi cechami w ocenie sensorycznej.

Na podstawie dokonanej charakterystyki chromatograficznej wnioskuje się, że niskie oceny sensoryczne niektórych badanych destylatów wynikają głównie z nadmiernej zawartości w nich alkoholu heksylowego (rys. 1) oraz stosunkowo niewielkiej obecności estrów ogółem w odniesieniu do ilości octanu etylu (tab. 2). Szczególne znaczenie może mieć mniejsza zawartość w tych destylatach takich estrów, jak: octan izoamylu, octan n-amylu, propionian izoamylu oraz walerian etylu i walerian izopropylu. Określoną rolę w zmniejszeniu cech sensorycznych destylatu A (tab. 1) ma również nieobecność w tej próbie kwasu enantowego i związku niezidentyfikowanego (prawdopodobnie kwas mirystynowy) z jednocześnie większą o ok. 40% w stosunku do próby E. zawartością kwasu octowego (rys. 3).

Stwierdzono również, że pomocnymi wskaźnikami oceny destylatów z gruszek mogą być niektóre wartości wynikające z obliczeń (tab. 2), a głównie estry ogółem minus estry obliczone oraz estry ogółem minus octan etylu. Dodatnia wartość pierwszego wskaźnika, zwłaszcza powyżej 5,0, wskazuje na zachowanie pozytywnych proporcji pomiędzy kwasami i estrami w destylatach. Różnica wynikająca z zawartości estrów ogółem i octanu etylu kształtowała się w destylatach z wysoką oceną punktową powyżej 250 mg/dm^3 100°.