Review article

Institute of Brewing & Distilling

Received: 28 January 2015 Revised: 2 November 2015 Accepted: 2 November 2015 Published online in Wiley Online Library: 6 January 2016

(wileyonlinelibrary.com) DOI 10.1002/jib.288

The analysis of raw spirits – a review of methodology

Paulina Wiśniewska,* Magdalena Śliwińska, Tomasz Dymerski, Waldemar Wardencki and Jacek Namieśnik

Agricultural distillates (raw spirits) are alcoholic liquids obtained through distillation (preceded by alcoholic fermentation) of specific agricultural products that do not have the properties of ethyl alcohol or a spirit, but still retain the aroma and taste of the raw ingredients used. This review is a brief overview of agricultural distillates and of some methods commonly used (GC-MS, GC-FID, GC-O, electronic nose) for performing quality assessments and for determining the composition and botanical origins of the raw spirits. Copyright © 2016 The Institute of Brewing & Distilling

Keywords: agricultural distillates; raw spirits; gas chromatography; electronic nose; botanical origin

Introduction

Alcoholic beverages are divided into beers, wines and spirits prepared with the use of ethyl alcohol of agricultural origin. According to European regulations *(1)*, an agricultural distillate is an alcoholic liquid obtained through distillation (preceded by alcoholic fermentation) of specific agricultural products, which does not have the properties of ethyl alcohol or a spirit, but still retains the aroma and flavour of the raw ingredients. If the product's label contains information regarding the raw material used (e.g. rye), said material can be the only one used to obtain the agricultural distillate. Owing to the diversity of raw materials, it is necessary to control the quality and botanical origin of substrates used in the production of agricultural distillates. It is the raw materials and the production method that influence, to a large extent, the composition of the raw spirits produced.

In this review groups of chemical compounds found in agricultural distillates are described in detail. Also presented here are studies conducted by means of various analytical techniques and aimed at determining the composition, quality and botanical origin of the raw spirits.

Characteristics of by-products

Ethyl alcohol of agricultural origin must fulfil specific requirements, such as:

- no detectable flavour other than that of the raw material;
- alcohol content by volume no less than 96%;
- selected residues levels no greater than specified in Table 1 *(1)*.

Selected raw materials determine the composition of agricultural distillates obtained from them. However, the fermentation process and its conditions, *inter alia*, the type of fermentation tank also play a significant role with regard to modification of agricultural distillate composition *(2)*. Besides ethanol, yeast fermentation produces volatile and non-volatile by-products influencing the quality of the spirit. The following non-volatile substances can be found in the dry mash: unfermented sugars, cellulose, substances containing nitrogen compounds and mineral salts. During distillation, some substances remain in the fermentation mixture, for example, glycerin and acids such as lactic acid *(3)*. However most by-products end up in the agricultural distillate in the form of azeotropic mixtures resulting from mixing with water or alcohol *(3)*. The following groups of compounds are considered to be by-products: methanol, higher alcohols, esters, fatty acids, carbonylic compounds such as aldehydes, ketones and acetals and others *(2, 3)*. Concentrations of the aforementioned products are dependent, to a large extent, on the raw material used in the production of a given spirit. For example, studies have shown that raw spirits obtained from triticale contain relatively small amounts of acids, esters, methanol and higher alcohols compared with rye distillates *(4)*.

Higher alcohols

Higher-order alcohols are a group of by-products that negatively influence the quality of agricultural distillates. The basic components of this group are fusel alcohols, present in the amount of 0.1–0.7% relative to ethanol produced. Isoamyl alcohols (2-methyl-1-butanol, 3-methyl-1-butanol) constitute the largest part, while isobutanol and *n*-propanol are present in lesser amounts. It is worth mentioning that the ratio of 3-methyl-1-butanol to 2-methyl-1-butanol depends on the raw material used, that is, the ratio is equal to 1.1–1.7, 2.1–3.3 and 3.7–5.1 for molasses, grain and potato raw spirits, respectively *(3)*. Fusel alcohols, characterized by an unpleasant, choking smell, are almost entirely removed during distillation and rectification as their boiling point is higher than that of ethanol. A high content of fusel alcohols causes the obtained product to taste and smell similar to a 'moonshine' product. On the other hand, a moderate amount of fusel alcohols is desired in some alcoholic beverages, such as cognac and brandy *(5)*.

* Correspondence to: P. Wiśniewska, Department of Analytical Chemistry, Gdansk University of Technology, Narutowicza St 11/12 , Gdańsk 80-233, Poland. E-mail: p.m.wisniewska@gmail.com

Department of Analytical Chemistry, Gdansk University of Technology, Narutowicza St 11/12, Gdańsk80-233, Poland

Table 1. Maximum level of selected residues *(1)*

Residue	Unit	Maximum level
Total acidity	Expressed in grams of acetic acid per hL of 100% vol. alcohol	1.5
Esters	Expressed in grams of ethyl acetate per hL of 100% vol. alcohol	1.3
Aldehydes	Expressed in grams of acetaldehyde per hL of 100% vol. alcohol	0.5
Higher alcohols	Expressed in grams of 2-methyl-1-propanol per hL of 100% vol. alcohol	0.5
Methanol	Expressed in grams per hL of 100% vol. alcohol	30
Dry extract	Expressed in grams per hL of 100% vol. alcohol	1.5
Volatile bases containing nitrogen	Expressed in grams of nitrogen per hL of 100% vol. alcohol	1.5
Furfural	—	Not detectable

Methanol

Methanol is a toxic compound, which can be lethal if consumed in an amount greater than 30–50 g *(2)*. The lowest dose reported to be lethal for oral exposure (LDLo) of methanol has been determined to be 143 mg/kg body weight for human *(6)*. It is present in all distillates of agricultural origin, except for those obtained from molasses. The least amount of methyl alcohol is found in grain distillates, and the largest in fruit distillates. Methanol is produced owing to the activity of pectinesterase, which is present in the raw materials and enzymatic preparations and the amount of which depends on the raw materials used *(3,7)*.

Esters

Esters in alcoholic beverages are formed during the condensation of acids and alcohols, mainly in the course of fermentation and aging. In general, the concentration of esters in raw spirits depends on the type of raw material, yeast strain used, microbiological cleanliness of the environment and the mash pH. Esters have a very low threshold of odour detection and an intense smell. The most frequently occurring ester is ethyl acetate. Low concentrations of ethyl acetate smooth out the harsh odour of some alcoholic beverages, while its presence at high concentrations lends a so-called 'vinegar flavour' to products *(2, 3)*.

Fatty acids

Fatty acids occur in alcoholic beverages in slight amounts. They have, however, a relatively low odour detection threshold. The presence of fatty acids is undesirable as they give beverages a soapy flavour. Caproic acid, caprylic acid, miristic acid and lauric acid are the most frequently occurring fatty acids *(2)*. It has been observed that palmitic acid, lauric acid, stearic acid and oleic acid accumulate in yeasts and therefore can be transferred into agricultural distillates in large amounts via yeast fermentation *(3)*.

Carbonylic compounds

Carbonylic compounds present in raw spirits are mainly produced during the fermentation process; their amount is influenced by, *inter alia*, the type of raw material used, yeast strain, pH, temperature and sugar concentration. The following carbonylic compounds are most frequently found in raw spirits: formaldehyde, acetaldehyde, butyraldehyde, isobutyraldehyde, propionaldehyde, crotonaldehyde, pentanal, isopentanal, hexanal, 2-butanon, furfural, diacetyl, acetylacetone, acrolein, acetone and glyoxal. Most of the aforementioned compounds cause an unpleasant taste and odour in spirits even when present at low concentrations, while acrolein is strongly carcinogenic and irritating to the eyes and to the respiratory system *(3,5)*.

Analysis of agricultural distillates

Owing to complexity of the matrix, distillates of agricultural origin pose a challenge for analytical chemists. They contain, apart from ethanol, which is the main component, low concentrations of various other compounds from different groups. Analysis of these distillates is of utmost importance not only because of the legal requirements that need be fulfilled in order to use them in the production of spirit-based beverages, but also because of the plethora of compounds influencing the quality of said beverages. As mentioned above, the presence of by-products such as aldehydes, acids, esters and higher alcohols influences the aroma and flavour of the agricultural distillate. Therefore, in order to monitor product quality and the production process, it is important to test for the presence of these compounds. All tests described below are also listed in Table 2.

In order to assess the quality of a raw spirit, the content of acrolein is often determined. Acrolein is the simplest unsaturated aldehyde and it is carcinogenic, toxic and strongly irritating to mucous membranes, eyes and the upper respiratory tract. The analysis of agricultural distillates obtained from potatoes and grain (rye) via unmodified and modified fermentation processes is described by Kotarska et al. *(8)*. High concentrations of acrolein were observed in both the potato mash and grain mash prior to the introduction of a modified fermentation. The measured concentrations of acrolein in low-quality rye raw spirits ranged from 0.095 to 0.164 mg/dm^3, while in the potato raw spirits concentrations ranged from 0.071 to 0.200 mg/dm^3. The level of acrolein decreased following a modification of the procedure, namely, after the acidity of yeast growth medium had been adjusted. Distillates of agricultural origin were analysed using gas chromatography.

Pyrazines are heterocyclic aromatic compounds containing a six-membered ring with two nitrogen atoms in positions 1 and 4, and they occur naturally in vegetables and insects. Pyrazines are the products of primary and secondary metabolic processes that take place in some microorganisms. In the case of agricultural distillates, pyrazines are the products of the Maillard reaction, which occurs when thermal processing is not optimal. Testing for the presence of pyrazines can be performed by means of gas chromatography coupled with mass spectrometry (GC-MS) with flame-ionization detection (FID).

Kłosowski and Błajet-Kosicka *(9)* describe how samples were collected at a distillery that employs a high-pressure steaming method for starch release from the cellular structures of raw

Table 2. Examples of the application of different analytical techniques for analysing distillates of agricultural origin

Sample type	Analysed compound	Selected technique	Reference
Rye distillate, potato distillate	Content of acrolein	GC	*(8)*
Corn distillate	Content of pyrazines	GC-FID, GC-MS	*(9)*
Potato distillate	Content of aldehydes during fermentation	GC-FID	*(10)*
Grain distillate	Content of esters	GC-FID, GC-MS	*(11)*
Grain distillate	Quality evaluation	GC-MS	*(12)*
Corn distillate	Impact of mycotoxin-contaminated corn on the composition of agricultural distillate	GC-FID	*(13)*
Grain distillate	Quality evaluation	GC-MS, GC-O	*(14)*
Grain distillate	Quality evaluation	GC-O	*(15)*
Distillate made from unmalted rye and different malts	Quality evaluation	GC-MS	*(18)*
Grain distillate	Quality evaluation	e-nose	*(19)*
Triticale, corn, rye, wheat and barley distillate	Quality evaluation	e-nose	*(23)*
Potato distillate, rye distillate, corn distillate	Distinguishing among botanical origins	GC-FID, MS-nose	*(24)*
Potato distillate, rye distillate, corn distillate	Distinguishing among botanical origins	GC-FID, GC-MS	*(25)*
Corn distillate, wheat distillate, triticale distillate, rye distillate	Distinguishing among botanical origins	GC-MS	*(26)*
Triticale, corn, rye, wheat and barley distillate	Distinguishing among botanical origins	e-nose	*(27)*
Distillates of natural and synthetic origin	Identifying the origin	GC-FID	*(28)*

material by means of a Henze steamer. The corn distillate originating from the aforementioned distillery was characterized by relatively high concentrations of 2,5-dimethylpyrazine and 2,3,4,5-tetramethylpyrazine. The samples subjected to overly intense thermal treatment and the agricultural distillates from a mash obtained under modified temperature and pressure conditions were analysed. After optimization of the steaming process, the samples so obtained contained lower concentrations of pyrazine derivatives, while the efficiency loss of ethanol production dropped to as low as 0.85 dm^3/100 kg. This indicated that the monitoring of pyrazine formation in agricultural distillates could be a reliable source of information about the correctness of the technological process applied *(9)*.

As mentioned above, carbonylic compounds have a negative impact on the quality of raw spirit. It is therefore very important to control the level of these compounds in agricultural distillates during the production process. Czupryński and Kotarska *(10)* addressed this issue in studies of potato agricultural distillates. The enzymes, Maxamyl (a bacterial α-amylase) and Amigase (an amyloglucosidase), as well as D-2 yeasts, were used in these investigations *(10)*. Two fermentation processes, differing by their initial temperature value, were conducted at 31 and 28°C. The collected samples were analysed by means of GC-FID. For the two fermentation processes, the concentration of carbonylic compounds after 8 h equalled 213 and 231g/dm^3, respectively. Both these values exceeded the permissible level of carbonylic compounds as defined by the Polish standard (i.e. 0.1 g/dm^3). Consecutive measurements were performed after 22 and 72 h of fermentation. It was finally concluded that the level of aldehydes decreased to 0.05 g/dm^3 for both temperature settings *(10)*.

Ethyl esters significantly influence the aroma of agricultural distillates. These compounds are difficult to determine owing to the fact that they are present in raw spirits at low concentration levels. Therefore finding a suitable method for determining ethyl esters is of high importance. Ten samples of grain distillates of agricultural origin from a Polish distillery were tested by Plutowska and Wardencki *(11)* for the presence of the following esters: ethyl acetate, ethyl propanoate, ethyl butyrate, ethyl pentanoate, ethyl hexanoate, ethylheptanoate, ethyl octanoate, ethyl, nonanoate, ethyl decanoate, ethyl undecanoate, and ethyl dodecanoate. Samples were prepared using solid-phase microextraction (SPME), including technique optimization by, *inter alia*, fibre selection. In the end, the DVB/CAR/PDMS fibre was chosen. Samples thus obtained were then analysed by means of GC-FID and GC-MS. These techniques made it possible to determine the aforementioned esters at μg/L concentrations *(11)*.

Apart from compounds and compound groups described above, the matrix composition of agricultural distillates was also investigated by Plutowska et al. *(12)*. Such studies were performed on samples of grain distillates originating from Polish distilleries. As a result, 13 samples of good quality and 13 samples of poor quality were analysed. The analysis was conducted using GC-MS. Samples were prepared via headspace (HS)-SPME. The largest group of compounds detected were esters, which play a significant role in forming the agricultural distillate aroma. Higher alcohols and aldehydes were the next most important group, which however have a negative impact on the aroma of spirit-based beverages. It should be noted that the richer the aroma profile, the lower the quality of agricultural distillates. Efforts were made to obtain neutral distillates of agricultural origin devoid of compounds such as aldehydes. In the case of distillates of poor quality, significantly more of these compounds were detected compared with the high-quality raw spirits *(12)*.

By using gas chromatography coupled with a FID, it was possible to determine the impact of mycotoxin-contaminated grain on raw spirit *(13)*. Mycotoxins are produced by certain species of mould and fungi. These toxins are often carcinogenic and can rarely be spotted with the naked eye on the grain. Kłosowski and Mikulski *(13)* describe the procedure for evaluating the influence of aflatoxins B_1, B_2, G_1 and G_2, ochratoxin A, zearalenone, deoxynivalenol and fumonisin B_1 on agricultural distillates obtained from corn mash. It was found that all mycotoxins caused an increase in the acetaldehyde concentration by 30–100% with the exception of fumonisin B_1. Most mycotoxins did not influence the concentration of higher alcohols. Fumonisin B_1 and ochratoxin A were an exception as they caused a decrease in the 2-methyl-1-butanol concentration in the distillates of agricultural origin. Deoxynivalenol caused a decrease in the ester content (by 32%), while ochratoxin A increased the concentration of esters. In conclusion, the presence of mycotoxin-contaminated corn altered the composition of the agricultural distillates *(13)*.

The quality of raw spirits was investigated by Wardencki et al. *(14)* by means of GC-MS and gas chromatography-olfactometry (GC-O). Samples were prepared using SPME with the application of mixed coatings, that is, DVB/CAR/PDMS. Overall, 39 samples of agricultural distillates originating from Poland were analysed, which included 13 samples not fulfilling the Polish norm, 13 samples evaluated as average and 13 samples classified as being of the highest quality. The samples were analysed using two columns of different polarities. Over 100 compounds were recognized in the samples of poor quality, and the most frequently occurring compounds were identified. Next, all the samples were analysed by means of GC-O and their retention times were compared with those from the GC-MS analysis. Characteristic aromatic compounds allowing one to make the distinction between samples of different quality were selected. It was noted that the sample quality decreased with increasing richness of its aroma profile. This phenomenon was associated with the presence of acetals, esters, dimethyl trisulphide and geosmin. Besides the aforementioned substances, the volatile fraction of the low-quality raw spirits consisted of aldehydes, terpenes, thiophene, furan, xylene and guaiacol derivatives. By using GC-O, these compounds were identified as responsible for lowering the quality of the analysed raw spirits *(14)*.

The same samples were analysed again by Plutowska and Wardencki *(15)* with GC-O and sensory analysis, the latter conducted by a group of three panellists. The HS-SPME technique was used to prepare the samples prior to analysis. Based on the results of GC-O analysis, 15 of the most frequently occurring compounds were chosen and then fitted to specific aromas. Based on the published literature *(16, 17)*, nine sensory descriptors were used in the sensory analysis, namely: onion/vegetable, earthy/mouldy, bread/toast, fruity/sweet, chemical/solvent, nauseating, acrid/penetrating, green/plant and tart. A four-point scale was established according to which three points were equivalent to a very intense odour, two points indicated a medium strength odour, one point meant a low intensity odour, and zero points was equivalent to an undetectable odour. The results of the sensory analysis showed that the samples classified as having the most intense odour displayed the lowest quality. In those samples, the aromas such as earthy/mouldy, onion/vegetable, tart and acrid/penetrating were identified. The samples of the highest quality were characterized by three or four aromas, mainly nauseating, fruity/sweet, chemical/solvent and green/plant. It was established that geosmin and dimethyl trisulphide were responsible for the least pleasant smell *(15)*.

GC-MS was used by Balcerek et al. *(18)* to analyse agricultural distillates obtained from unmalted rye and different malts. Concentrations of the following compounds were determined: acetaldehyde, furfural, hexanal, benzaldehyde, ethyl acetate, ethyl butyrate, 3-methyl butyl acetate, hexyl acetate, ethyl caproate, ethyl caprylate, ethyl benzoate, methanol, 1-propanol, 2-methyl-1-propanol, 1-butanol, 2-methyl-1-butanol, 3-methyl-1-butanol, 1-hexanol and benzyl alcohol. The agricultural distillate from the unmalted rye was found to have the highest concentration of acetaldehyde and amyl alcohol isomers and the lowest concentration of furfural, while the raw spirits made from mashes containing cereal malts were characterized by lower concentrations of the undesirable acetaldehyde *(18)*.

Apart from GC, the analysed distillates of agricultural origin were evaluated with an electronic nose *(19)*. The electronic nose is an analytical tool designed for the rapid detection and identification of aromas by mimicking the mode of operation of the human olfactory system. To this end, specific chemical sensors are exposed to a gas mixture and generate a characteristic aroma profile that constitutes a so-called 'fingerprint' of this mixture. Mixture components are identified based on the comparison with the profiles of reference substances *(20, 21)*. In the case of quality evaluation of agricultural distillates, an electronic nose prototype constructed in the laboratory of one of the authors of the cited article and equipped with six MOS sensors was used. Obtained results were analysed by applying a chemometric method, that is, principal component analysis (PCA). The following parameters were optimized during the analysis: the temperature at which gas was sparged, volumetric gas flow and the duration of gas sparging. After determining the optimal conditions, a PCA graph was generated that allowed one to distinguish between agricultural distillates of various qualities by assigning them to one of three quality groups, that is, good, average or poor.

The same type of electronic nose was used for a quality assessment of agricultural distillates obtained from triticale, corn, rye, wheat and barley. For the purpose of data analysis linear discriminant analysis (LDA) and quadrant discriminant analysis (QDA) were used. Samples were classified into three quality groups: good, average or poor. During the LDA analysis, 97% of samples were classified properly, and during QDA analysis, 98.5% of the samples were classified into their appropriate groups. After applying a cross-validation method, in both cases 96. 3% of the samples were classified properly. This result suggested that this type of electronic nose prototype can be used in the future for the rapid analysis of agricultural distillates *(22)*.

Besides distinguishing between agricultural distillates in relation to their quality, studies aimed at identifying the botanical origin of such distillates were also conducted by Jeleń et al. *(23)*. Distillates of agricultural origin can be obtained from different raw materials, for example, grains (rye, triticale, corn, wheat) and agricultural plants such as potatoes. In order to identify the botanical origin of alcoholic beverages, stable isotope ratio analysis can be applied *(24)*. In addition to stable isotope ratio analysis, SPME-MS technique was employed, that is, mass spectrometry-based electronic nose and SPME. Overall, 138 samples of agricultural distillates were analysed, including 84 samples of rye distillates, 27 samples of corn distillates and 27 samples of potato distillates. All agricultural distillates were supplied by distilleries from the region of Greater Poland. The main contaminants present in distillates of agricultural origin were determined by means of GC-FID, while samples were prepared using the SPME technique. After testing five types of fibre, the DVB/CAR/PDMS fibre was selected as the most suitable. Data obtained with the mass spectrometry-based electronic nose was analysed by employing PCA and LDA. LDA analysis proved to be the best method for distinguishing between the three types of samples *(23)*. Another article by Ziółkowska and Jeleń *(25)* was based on the analysis of the aforementioned samples by applying GC-FID and GC-MS. The obtained data was also analysed by employing chemometric methods such as PCA and LDA. The application of GC-FID and PCA method only allowed for the identification of raw spirits produced from potatoes, likewise the application of LDA method. Potato raw spirits were classified as one group, while rye- and corn-based raw spirits were classified as another. GC-MS and PCA methods were not sufficient to distinguish any group of raw spirits. Better results were achieved by applying LDA method, which allowed for a relatively good distinction between corn raw spirits and potato raw spirits. The only problem was encountered while attempting to identify samples of rye-based raw spirits. Out of 84 samples two were misidentified as potato raw spirit and three as corn raw spirit *(25)*.

HS-SPME-GC-MS analysis was employed by Biernacka and Wardencki *(26)* to discriminate between raw spirits produced from wheat, triticale, rye and corn. Overall, 102 compounds belonging to esters, alcohols and acetals were identified. The percentage concentrations of specific compound groups that occurred in a given raw spirit type were compared. Based on the conducted research, it was concluded that esters were a dominant group. Compared with other agricultural distillates, corn-based raw spirits contained the highest amount of esters (92%). In other agricultural distillates, esters were present at a level lower than 80% of the total number of identified compounds. Acetals were present in all grain raw spirits at a level of ca. 3%, while the content of higher alcohols reached 10% in wheat raw spirits, 9% in triticale- and rye-based distillates and 1% in corn distillates. Moreover, researchers identified 12 compounds that can be considered as potential botanical markers (1,1,3-triethoxypropane, 2,5-dimethylfuran, 2-butylfuran, 2-pentylfuran, butan-2-ol, propyl decanoate, furfural, 2-methylpropyl acetate, hexyl acetate, propyl acetate, propyl octanoate and ethyl propanoate). Canonical discriminant analysis was used to compare the samples. Obtained results allowed for the discrimination of three groups of agricultural distillates, that is, the triticale group, the wheat group and the combined corn/rye group *(26)*.

An electronic nose based on ultra-fast gas chromatography was used by Wiśniewska et al. *(27)* for quick differentiation between agricultural distillates based on their botanical origin. Samples included agricultural distillates from rye, triticale, wheat and corn. For data analysis PCA, discriminant function analysis, SIMCA (soft independent modelling of class analogies) and Statistical Quality Control were used. Only discriminant function analysis and SIMCA analysis allowed differentiation between agricultural distillates based on their botanical origin *(27)*.

Besides identification of botanical origin, research aimed at finding a method of distinguishing between natural and synthetic ethanols was also conducted by Vyazmina and Savchuk *(28)* employing GC-FID analysis. The content of selected compounds, as markers of natural and synthetic alcohols, was determined. Obtained results showed that the selected compounds allowed one to distinguish between raw spirits of natural and synthetic origin *(28)*.

Summary

Owing to the complex composition of the distillate matrix, the analysis of raw spirits poses a significant challenge. This is because agricultural distillate samples contain high ethanol concentrations and relatively low to only trace-level amounts of other compounds. Owing to the slight amount of some of these compounds in agricultural distillates, it is necessary to analyse the samples using advanced analytical equipment that is characterized by versatility and high sensitivity. Until now, raw spirits were most commonly analysed using gas chromatography. This is due to the fact that volatile organic substances constitute the majority of the components in such samples. Agricultural distillates must be subjected to comprehensive testing in order to determine their quality, complex composition and botanical origin. The analysis of raw spirits is of utmost importance because it is further used in the production of alcohols such as vodka. Therefore the quality control of the raw spirits should be conducted during the production process. To date, a relatively low number of scientific articles tackling the matter of agricultural distillates have been published. In this review, a group of compounds present in agricultural distillates, and the related research conducted by means of different analytical techniques and aimed at determining the composition, quality and botanical origin of raw spirits have been described. This has allowed for the compilation in a single body of work of the information pertaining to the composition of agricultural distillates, which will prove useful in further discussion on this subject.

Acknowledgements

The authors acknowledge the financial support for this study by the grant no. 522 2012/05/B/ST4/01984 from National Science Centre of Poland.

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