Changes in the Major Volatile Compounds of Cider Distillates During Maturation

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Principal aroma components in cider distillates were determined by gas chromatography with direct sample injection; the method described was found to be reliable. Acetaldehyde decreased during aging, which could be a consequence of the interaction of this molecule with ethanol, since an increase of acetal level was detected. A higher concentration of methanol was observed in spirits obtained from cider made from apple juice concentrate; this fact could be due to the intense enzymatic treatment (liquefaction) employed in manufacturing of apple juice concentrate. The system for concentrating apple juice might foster a higher level of furfural in the distillates manufactured from cider obtained from apple juice concentrate than the spirits made from traditional cider; the level of this carbonyl component increased during aging. The higher alcohol level rose throughout maturation; this fact could probably be explained by the acid-catalysed transesterification reaction. When cluster and factor analyses were employed, 'natural' groupings among the spirits under study were obtained on the basis of the raw material and aging time.

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Introduction

Cider brandy, obtained by the distillation of cider made from cider-apple cultivars, is a common drink in Western European regions where, because of peculiar climatic characteristics, grape-vine cultivars are not viable. In these countries, cider brandy is considered a high quality product and a factor of important economic repercussion. Production of this alcoholic product can be grouped into at least three distinct stages consisting of: (i) selection and processing of the apples, (ii) fermentation and distillation processes, and (iii) maturation of the distillate in oak barrels to produce the final aged brandy.

Obviously, an adequate selection of raw materials and convenient methods of manufacture determine the organoleptic characteristics of the cider brandy obtained. Among the different substances that determine the specific flavour of distillate spirits, volatile compounds are the most important. Analysis of these substances allows characterization of the drink. In fact, Beech and Carr (1) showed that cider-apple cultivars present differences in relation to the levels of low-temperature boiling compounds. On the other hand, typical aromatic compounds (alcohols, esters, allyl derivatives, etc.) have been associated with apple-like odours (2,3). Furthermore, this analysis has allowed researchers to establish the influence of manufacturing technology on the quality of the final product, as the aroma depends more on technological parameters (4)

in addition to maturation in wood barrels (5,6), than on the raw material, since volatile compounds are formed during fermentation, distillation and aging from their precursors.

There is no doubt that gas chromatography (7,8) is the best technique for analysis of volatile compounds. Gas chromatographic examination of fractions obtained from distilled spirits by different extraction systems (9,10) has revealed the presence of more than 200 volatile constituents. However, a simple technique was required for technological and fingerprinting purposes, based on the major constituents which could readily be determined by direct injection (11).

The purpose of this work was to elaborate a simple chromatographic method for the determination of the major volatile components in cider brandies during their fabrication, and to find out which of them can be employed for classifying the spirits on the basis of the raw material and aging time.

Material and Methods

Raw material

Two types of cider were used for making the spirits: cider produced by traditional technology (A) and cider obtained from apple juice concentrate (B). The traditional cider was prepared from the juice of a mixture of cider apples: bitter 0.01, sharp 0.33, sweet 0.30, bitter-sweet 0.03 and mildly-sharp 0.33, with different sensory properties endowing an overall acidic nature to the

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resulting juice. These varieties were classified according to the criteria described by Dapena (12) for Spanish apple cider varieties and Beech and Carr (13) for English apple cider cultivars. The mixture was processed in a pilot plant which included the following steps: milling with a hammer mill and slow pressing with a batch mechanical press (4 d pressing time). The fermentation process was then conducted by wild microflora. In the case of the type B cider, an apple juice concentrate made by means of a liquefaction system was used; the fermentative process was carried out using *Saccharomyces cerevisiae* as a starter. The alcohol content was 60 mL/L for traditional cider and 80 mL/L for cider made from apple juice concentrate.

Distillation

The batch distillation system was employed for distilling both ciders. The copper wash-still distillation vessel capacity was 500 L and steam was used as the heat source. The volatile compounds obtained inside the first vessel of the still were carried to the rectifying column, which had 16 bubble-cap plates; 1150 L of traditional cider and 1760 L of type B cider were employed in the making of the spirits. Alcoholic degree of the spirits was monitored during the distillation process. Three fractions of spirits, namely heads, heart and tails, were separated on the basis of their alcoholic contents. The volume of heads obtained was 0.01 of the volume of cider employed (250 L), the average alcohol content of the heart fraction was 650 mL/L for distillates obtained from traditional cider and 620 mL/L in the case of the type B cider; the tails produced (average alcohol content 300 mL/L) were employed in following distillations. All heart fractions obtained were subjected to an aging process in American oak barrels with a capacity of 35 L each for 12 months; five samplings were carried out for analysis every 3 months. Experiments on aging of the spirits were performed in triplicate (type B) or duplicate (type A).

Reagents

Standards of analytical quality were supplied by Fluka (Busch, Switzerland) and Sigma-Aldrich (Madrid, Spain). Standard solutions were prepared in EtOH/Water (65/35).

Gas chromatography (GC)

The following instrument and column were used for analytical GC: a Hewlett-Packard 5890 gas chromatograph fitted with a flame ionization detector and 5 m × 3.2 mm stainless steel column packed with carbowax 1500 on carbopack C 8/100. The column was operated isothermally at 40°C for 14 min and then programmed at 1.0°C/min to 60°C, 1 min at 60°C, and was finally programmed at 2.5°C/min to 120°C. Helium (518 KPa) was used as the carrier gas. Injector and detector temperatures were maintained at 170°C. The injection volume was 1 µL.

Statistical analysis

Repeated measures of analysis of variance have performed with a Greenhouse-Geisser and a Huynh-Feldt fitting was carried out using the SAS (14) statistical package; two factors were considered in this study, namely technology (cider type) and aging (maturation in oak wood barrels). Data matrix was analysed by principal components analysis, and cluster analysis (15). The multivariate analysis was carried out on 22 samples (spirits obtained from two technologies and with different aging) using 14 variables (major volatile compounds).

Results and Discussion

Optimization of the analytical method

Figure 1 shows the GC separation of the aroma components using the above mentioned method. Compounds were identified by comparing the retention time of the GC peak with authentic compounds. We monitored changes in each of the volatile compounds (acetaldehyde, methanol, acetone, ethyl acetate,

Fig. 1 Chromatogram of a synthetic solution of volatile compounds: (1) acetaldehyde; (2) methanol; (3) acetone; (4) ethyl formate; (5) ethanol; (6) ethyl acetate; (7) 1-propanol; (8) 2-butanol; (9) i-butanol; (10) ethyl propionate; (11) 1-butanol; (12) 3-pentanol (internal standard); (13) acetal; (14) D-amyl alcohol; (15) i-amyl alcohol; (16) furfural; (17) i-amyl acetate; (18) 1-hexanol. Chromatogram obtained in a 5 m × 3.2 mm stainless steel column packed with carbowax 1500 on carbopack C 8/100. Temperature program: 40°C for 14 min, raised to 60°C at 1.0°C/min, 1 min at 60°C and raised to 120°C at 2.5°C/min

Table 1 Recovery studies of volatile compounds added to cider brandy

Compound	Cider brandy	Amount in brandy ^a (mg/L)		Amount added (mg/L)	Found ^a (mg/L)		% Recovery
		$\bar{x}$	s_x		$\bar{x}$	s_x	
Ethyl formate	A	41.8	1.2	18.3	59.5	0.6	96.7
				45.9	85.3	4.0	94.8
				91.7	135.0	1.1	101.6
	B	78.3	5.9	45.9	119.8	3.1	90.4
				91.7	161.9	3.1	91.2
				183.4	263.6	4.0	101.0
	C	22.1	8.2	45.9	63.3	6.9	89.8
				91.7	109.6	7.0	95.4
				183.4	189.9	1.9	91.5
Ethyl acetate	A	1,700.6	1.1	1,704.8	3,250.1	1.0	90.9
				3,288.7	4,687.8	4.0	90.8
				4,993.5	6,535.6	0.6	96.8
	B	3,513.6	1.0	1,262.8	4,650.1	1.0	90.0
				1,804.0	5,376.5	0.6	103.3
				3,608.0	6,830.2	1.1	91.9
	C	449.9	4.6	90.2	548.3	3.9	109.1
				180.4	632.7	2.7	101.3
				360.8	801.0	2.0	97.3
Ethyl propionate	A	102.4	0.9	17.8	118.9	1.1	92.7
				44.6	148.1	2.8	102.5
				89.1	189.6	1.0	97.9
	B	91.5	3.4	44.6	131.3	1.4	89.2
				89.1	176.1	3.1	94.9
				440.2	567.9	1.6	108.2
	C	14.4	6.2	59.7	79.8	1.0	109.5
				178.2	177.0	5.4	91.2
				270.0	273.6	1.0	96.0
Methanol	A	411.2	0.8	79.1	492.5	4.9	102.8
				158.2	555.8	1.6	91.4
				316.4	711.8	1.9	95.0
	B	436.5	3.1	79.1	517.6	2.2	102.5
				158.2	592.3	1.7	98.5
				395.5	836.9	3.0	101.2
	C	547.6	3.2	79.1	627.3	1.9	100.8
				158.2	702.1	0.7	97.7
				316.4	889.7	4.1	108.1
2-Butanol	A	356.3	2.4	80.8	431.8	1.9	93.4
				202.0	548.2	2.6	95.0
				404.0	721.2	2.0	90.3
	B	404.8	4.6	80.8	487.7	1.3	102.6
				161.6	568.3	2.8	101.2
				404.0	827.9	1.6	104.7
	C	52.0	2.4	280.4	362.0	2.5	110.6
				390.3	483.3	1.8	110.5
				590.7	695.9	1.4	109.0
1-Propanol	A	513.7	0.7	80.4	589.9	0.8	94.8
				160.7	667.9	0.9	96.0
				321.4	823.5	1.6	96.4
	B	386.0	5.9	80.4	464.9	2.7	98.1
				160.7	540.7	1.9	96.3
				401.8	788.0	1.6	100.0
	C	306.1	2.0	80.4	382.1	3.5	94.5
				160.7	465.6	2.8	99.3
				321.4	643.0	2.7	104.8

Table 1 (Continued)

Compound	Cider brandy	Amount in brandy ^a (mg/L)		Amount added (mg/L)	Found ^a (mg/L)		% Recovery
		$\bar{x}$	s_x		$\bar{x}$	s_x	
i-Butanol	A	363.1	5.1	80.2	448.7	1.1	106.7
				160.4	517.0	0.3	95.9
				320.7	661.5	1.7	93.0
	B	290.0	4.7	80.2	372.1	2.0	102.4
				160.4	443.9	1.8	95.9
				400.9	694.1	3.8	100.8
	C	323.9	2.0	80.2	401.7	0.9	97.0
				160.4	480.6	1.3	97.7
				320.7	653.5	3.0	102.8
1-Butanol	A	123.2	2.4	809.8	910.6	3.6	97.2
				1,599.4	1,723.0	0.9	100.0
				2,559.0	2,761.2	0.3	103.1
	B	91.6	2.6	219.5	316.4	2.7	102.4
				374.9	506.2	1.1	110.6
				540.1	659.8	1.3	105.2
	C	106.9	5.9	40.5	143.3	0.6	89.9
				81.0	184.4	6.2	95.7
				162.0	258.1	3.6	93.3
D-Amyl alcohol	A	414.9	0.7	81.1	492.5	0.8	95.7
				162.2	565.7	1.2	93.0
				324.4	715.1	0.5	92.5
	B	313.9	3.3	81.1	402.1	1.2	108.8
				162.2	471.7	2.3	97.3
				405.5	739.4	3.1	104.9
	C	290.3	6.3	81.1	371.7	4.4	100.4
				162.2	450.9	2.6	99.0
				324.4	654.6	3.5	112.3
i-Amyl alcohol	A	2,072.5	4.6	809.2	2,921.8	1.0	105.0
				1,618.4	3,760.2	0.3	104.3
				3,236.8	5,620.0	3.2	109.6
	B	1,538.6	3.8	1,132.9	2,711.4	0.6	103.5
				1,618.4	3,289.9	0.5	108.2
				3,236.8	4,966.6	0.9	105.9
	C	1,255.3	3.8	2,020.6	3,319.3	4.8	102.1
				3,121.1	4,483.0	3.5	103.4
				5,321.3	6,906.0	5.2	106.2
Acetaldehyde	A	331.7	8.6	222.8	540.3	2.8	93.6
				334.2	687.1	1.8	106.3
				557.0	938.3	3.2	108.9
	B	241.7	3.6	224.0	463.1	6.3	98.8
				336.0	581.6	6.1	101.2
				560.0	804.3	1.0	100.5
	C	119.0	9.5	208.8	338.8	4.5	105.3
				313.2	418.5	4.3	95.6
				522.0	619.2	6.2	95.8
Acetal	A	218.3	8.1	180.4	397.3	3.6	99.2
				451.0	630.2	3.9	91.3
				500.0	768.7	5.4	110.1
	B	338.0	3.7	213.2	557.7	10.0	103.0
				319.8	675.3	0.7	105.5
				533.0	917.0	1.0	108.6
	C	160.3	2.5	209.6	366.0	6.2	98.1
				314.4	451.8	8.4	92.7
				524.0	629.0	7.7	89.4

Table 1 (Continued)

Compound	Cider brandy	Amount in brandy ^a (mg/L)		Amount added (mg/L)	Found ^a (mg/L)		% Recovery
		$\bar{x}$	s_x		$\bar{x}$	s_x	
i-Amyl acetate	A	—	—	—	—	—	—
				99.9	124.6	0.5	92.8
	B	31.9	3.5	221.6 462.5	253.5 530.0	0.8 3.7	100.0 107.7
Acetone	C	—	—	—	—	—	—
				1.1	4.4	5.2	90.9
	A	3.4	5.8	2.8 5.6	5.8 9.1	3.7 5.0	85.7 101.8
	B	2.3	5.7	1.2 3.0 5.9	3.3 5.1 8.1	5.3 1.9 2.2	83.3 93.3 98.3
				1.3	4.5	3.0	100.0
	C	3.2	1.1	3.3 6.6	6.2 9.9	5.0 1.7	90.9 101.5
Furfural	A	91.6	1.7	22.3 44.6 111.4	111.5 135.2 199.8	5.9 4.2 2.3	89.2 97.8 97.1
				23.8	114.7	2.1	92.9
	B	92.6	6.9	47.5 118.8	133.2 192.2	1.4 4.0	85.5 83.8
				5.3	19.0	7.4	109.4
	C	13.2	8.5	10.6 21.2	25.4 35.8	4.4 5.1	115.1 106.6

^aMean values ($\bar{x}$) and relative standard deviations (s_x).

1-propanol, i-butanol, ethyl propionate, 1-butanol, acetal, D-amyl alcohol, i-amyl alcohol, furfural, i-amyl acetate and 1-hexanol) during aging of the spirits. Recovery studies were carried out in order to determine the accuracy of the method; 3-pentanol was used as an internal standard. Quantification was carried out directly by injection of 1 μ L of each sample, in triplicate, before and after adding known amounts of different volatile compounds. Three concentration levels of spiked volatiles were analysed. As can be seen in **Table 1**, the average recoveries ranged between 83% and 115%. The relative standard deviation for the three replicates of each sample was usually less than 7%.

Analytical control of volatile components during aging

The acetaldehyde content is closely linked with the distillation system employed; separation of different fractions during the distillation process is highly critical in relation to the percentage of acetaldehyde recovered, since this component occurs in the head fraction of the distillation.

As can be seen in **Table 2**, this aldehyde decreased during controlled step aging ($P < 0.01$), and a higher level was detected ($P < 0.01$) in the case of the spirits obtained from traditional cider (A). Throughout maturation, acetaldehyde is produced directly from ethanol, but it is then oxidized into acetic acid, and its interaction with ethanol resulting in the production of acetal should be taken into consideration. In fact, we

detected a significant ($P < 0.05$) increase of acetal during aging; on the other hand, a higher acetal level in distillates made from type A cider was observed ($P < 0.01$) which could be linked with the greater acetaldehyde content detected in said distillates.

The methanol concentration decreased ($P < 0.05$) in all samples (**Table 2**) probably as a consequence of different simultaneous processes: diffusion, evaporation, oxidation to formaldehyde, esterification and acetal transformation. It is generally accepted that methanol is not a byproduct of microorganism's fermentation, but that its occurrence is due to hydrolysis of pectic substances. We found a higher methanol level ($P < 0.01$) in B spirits, which could be explained by the intense enzymatic treatment (liquefaction) used for making apple juice concentrate.

Acetone is a metabolite of the pyruvate transformation developed during the process of making alcoholic beverages. The concentration detected in the spirits tested is in accordance with the results described by Nykänen and Suomalainen (16).

The distillation system and the raw material can be determining factors of the furfural percentage found in unaged spirits; in fact, furfural was only detected in the unaged B spirit, which may be due to the system of concentration (evaporation) usually employed for making apple juice concentrate. An increase ($P < 0.01$) in this carbonyl compound during aging was observed for all samples tested; this fact might be linked to the thermal treatment of the wood barrels, which promotes

degradation of the polysaccharides (17); on the other hand, significant differences were not detected between the two types of spirits, except for the last stage of aging (**Table 2**).

Changes in the amounts of amyl alcohols (D-amyl and i-amyl) during cider brandy maturation were detected. As can be seen in **Table 2**, the amyl alcohols content increased ($P < 0.01$; $P < 0.05$) during the oak maturation stage, which could be explained on the basis of the acid-catalysed transesterification reaction resulting from the nucleophilic characteristic of the major component of the cider brandy, namely ethanol. In particular, the transesterification process should be considered in the case of B spirits, since ethyl acetate and i-amyl alcohol increased while i-amyl acetate decreased (**Table 2**).

Ethyl propionate, 1-butanol and 1-hexanol levels were

higher in the distillates made from fresh apple juice than from the type B ones (**Table 2**) ($P < 0.01$). Except for ethyl propionate, where a significant evolution in time was not found, a significant increase during aging ($P < 0.01$) was detected for 1-butanol and 1-hexanol (particularly in A distillates). An increase in these alcohols might be fostered by transesterification processes; moreover, i-butanol increased during aging ($P < 0.01$) in A distillates, and a higher level of 1-propanol ($P < 0.01$) was obtained in B distillates; the opposite was observed for i-butanol ($P < 0.05$).

Factor analysis of the internal structure

A large number of high correlations among the variables studied with high statistical significance was

Table 2 Average contents (mg/L) of the volatile components of cider brandies

Compound	Spirit	Significance of aging factor	Stage of maturity (months) ^a				
			0	1	2	3	4
Acetaldehyde	A	++	216.3(a)	187.9(b)	176.1(b)	180.6(b)	186.5(b)
	B	++	174.1(a)	160.2(b)	148.6(c)	142.4(d)	147.2(cd)
	**			**	**	**	**
Methanol	A	+	450.5(a)	420.5(b)	430.4(ab)	427.0(ab)	413.4(b)
	B	++	688.4(a)	648.3(b)	640.4(bc)	621.4(c)	589.8(d)
	**			**	**	**	**
Acetone	A	++	2.1(b)	2.5(a)	2.6(a)	2.5(a)	2.7(a)
	B	+	1.9(a)	1.8(b)	1.9(a)	1.9(a)	1.9(a)
	**			**	**	**	**
Ethyl acetate	A	++	2709.7(a)	2433.8(b)	2243.9(c)	2129.1(d)	2036.2(d)
	B	++	260.5(b)	247.4(c)	250.4(c)	262.1(b)	276.8(a)
	**			**	**	**	**
1-Propanol	A	n.s.	85.8(ab)	83.5(b)	88.2(ab)	87.4(ab)	90.0(a)
	B	n.s.	102.5(ab)	101.9(b)	102.6(ab)	103.6(ab)	104.8(a)
	**			**	**	**	**
i-Butanol	A	++	139.8(bc)	133.8(c)	142.2(b)	145.7(ab)	149.2(a)
	B	n.s.	128.6(ab)	126.7(b)	129.7(ab)	130.0(ab)	130.7(a)
	**			**	**	**	**
Ethyl propionate	A	n.s.	6.4(a)	6.2(a)	6.1(a)	6.3(a)	6.1(a)
	B	0.0	0.0	0.0	0.0	0.0	0.0
	**			**	**	**	**
1-Butanol	A	++	82.2(b)	78.7(c)	83.0(b)	87.0(a)	88.4(a)
	B	++	9.2(d)	9.6(c)	10.5(a)	10.0(b)	10.2(b)
	**			**	**	**	**
D-Amyl alcohol	A	++	165.8(d)	160.4(c)	176.1(b)	183.5(a)	187.3(a)
	B	++	150.0(c)	149.6(b)	154.0(a)	152.6(a)	154.8(a)
	**			*	*	**	**
Acetal	A	+	104.3(bc)	133.9(c)	173.7(ab)	189.2(a)	191.9(a)
	B	n.s.	91.0(b)	106.5(b)	131.7(ab)	142.1(ab)	138.2(a)
	**			n.s.	**	**	**
i-Amyl alcohol	A	+	615.1(bc)	600.5(c)	641.2(ab)	653.8(a)	670.5(a)
	B	+	581.9(b)	581.6(b)	599.9(a)	597.4(ab)	605.5(a)
	**			*	n.s.	*	**
Furfural	A	++	0.0(c)	16.3(b)	26.9(a)	29.1(a)	35.9(a)
	B	++	18.5(c)	24.8(c)	37.5(b)	42.8(ab)	46.0(a)
	**			n.s.	n.s.	n.s.	**
i-Amyl acetate	A	++	31.7(b)	32.0(b)	30.4(b)	36.6(a)	37.3(a)
	B	++	62.2(a)	59.9(b)	58.2(c)	56.5(d)	48.5(e)
	**			**	**	**	**
1-Hexanol	A	++	44.1(c)	45.5(c)	51.0(bc)	60.2(ab)	68.2(a)
	B	n.s.	5.1(a)	2.7(b)	3.3(ab)	3.7(ab)	3.9(ab)
	**			**	**	**	**

n.s.=not significant.

* $P < 0.05$; ** $P < 0.01$ for technology factor.

+ $P < 0.05$; ++ $P < 0.01$ for aging factor.

§ Means with the same letter in parentheses are not significantly different.

Fig. 2 Two factorial axes projection of variables. (1) Acetaldehyde; (2) Methanol; (3) Acetone; (4) Ethyl acetate; (5) 1-Propanol; (6) i-Butanol; (7) Ethyl propionate; (8) 1-Butanol; (9) Acetal; (10) D-Amyl alcohol; (11) i-Amyl alcohol; (12) Furfural; (13) i-Amyl acetate; (14) 1-Hexanol

obtained from the correlation matrix; moreover, the determinant of the correlation matrix was very low. When Bartlett's test of sphericity was used, the null hypothesis was rejected ($\chi^2 = 809.02$; $P = 0.0000$). The Kaiser-Meyer-Olkin (KMO) measure of sampling adequacy was 0.86101, and the measures of sampling adequacy (MSA) obtained from the diagonal of the anti-image correlation matrix were higher than 0.7700; thus the data matrix could be considered as adequate for factor analysis according to Kaiser's criteria. The number of principal components (PC) was determined, having previously standardized the data from the correlation matrix. Two PC that accounted for 94.5% of the variance were chosen on the basis of Kaiser's criterion (eigenvalues higher than 1.0 being chosen). The percentage of variance of each variable explained by the two factors considered (communality) was

greater than 93% for all variables studied. On the other hand, the factorial model established could be appropriate for the treatment of the data taking in account the fact that all residuals obtained from the reproduced correlation matrix had absolute values smaller than 0.05.

As can be seen in **Fig. 2**, where the variables are projected on the plane formed by the two factors considered, the first eigenvector is closely related to 1-hexanol, 1-butanol, i-butanol, D-amyl alcohol, ethyl acetate, ethyl propionate and acetone due to high positive loadings; however, methanol, 1-propanol and i-amyl acetate are closely related to this component as a consequence of their high negative loadings. Furfural and acetal, on the other hand, are related to the second eigenvector (**Fig. 2**). Moreover, the results obtained by factor analysis were confirmed by cluster analysis of the

Fig. 3 Eigenvector projection of spirits

objects since two clusters were found and the samples were correctly classified; the first cluster consisted of spirits made from type B cider, and the second cluster included the cider brandy obtained from traditional cider (type A).

Figure 3 shows a projection of the observations on the plane formed by the first two components; as can be seen, the first component (eigenvector 1) allows us to differentiate between the spirits manufactured from different cider types, A and B, while the second component (eigenvector 2) is related to aging time, especially when distillates obtained from traditional cider were considered.

The scores for the first component are higher in type A than B spirits, and those with more aging time had higher scores than the young spirits for the second component (**Fig. 3**). Hence, the volatile compounds associated with the first principal component may be employed for classifying the spirits on the basis of raw material, although for a more precise conclusion with respect to this more samples should be considered.

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