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Comparative production of different melon distillates: Chemical and sensory analyses

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Abstract

Melon (*Cucumis melo* L.) fruits were crushed under different conditions, and the juice, pulp, and pastes obtained were fermented at two different pH levels (unadjusted and adjusted), at a pilot plant, to give an alcoholic content of 2.0–3.3% (v/v). The melon wines were double-distilled, the first distillation being in a reflux still, "alquitara", producing a distillate with an alcohol content between 18.5% and 25% (v/v). The second distillation took place in an alembic still, yielding a final alcohol content of 58–69% (v/v). Sixty volatile compounds were analysed by GC, and sensory evaluations were performed. The distillate made from one of the three substrates tested was rejected on the basis of the chemical and sensory analyses. The remaining distillates, from the other two substrates, were so similar that there were no preferences between them. Fermentation pH proved to be critical for the production of certain compounds (e.g., ethyl acetate and ethyl lactate) and hence for the sensory attributes of the final product. The melon distillates were compared with other commercial spirits.
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1. Introduction

Distillation of fermented fruit wines has been used in some countries for many years to obtain palatable beverages with high alcohol contents. Melons are a major crop in the Castilla-La Mancha region of Spain, and the large crop size results in high levels of surplus production. Research into the production of melon spirit was therefore commenced with a view to providing an additional outlet that would prevent wastage. The process of developing a new product has to be undertaken step by step, and for that reason trials to examine fruit processing, clarification, fermentation, column and alembic distillations were performed on laboratory and semi-pilot plant scales in the 1999 and 2000 seasons (Briones, Hernández Gómez, & Ubeda, 2002; Hernández Gómez, Úbeda, & Briones, 2003). Further work, performed in 2001, was carried out on a pilot plant scale using the best parameter values obtained earlier.

The aim of this study was to perform chemical and sensory analyses of the different distillates produced on a pilot plant and to compare the results with those from previous years and thus narrow down the production processes. At the same time, the volatile compounds in the distillates were compared with those in other commercially-available spirits.

2. Materials and methods

2.1. Fruit juices

"*Piel de sapo*" and "*Ruidera*" melon varieties were collected from the La Mancha region in Spain, in 2001,

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and processed in a pilot plant as previously described Hernández Gómez et al. (2003), yielding three different types of substrate for fermentation. The three substrates were melon "juice", "paste without skin" (pws), and "paste with skins" (paste) (Hernández Gómez et al., 2003).

Processing yields were calculated by weighing the raw material, the manufacturing waste (rinds and seeds) and the final substrate.

Conventional parameters, such as °Brix (using a hand-held refractometer) and pH (using the potentiometric method) were measured for each substrate type (juice, pws, and paste) (Table 1) according to *Recueil des Méthodes Internationales d' Analyse des Vins* [*Compendium of International Methods of Analysis of Wine and Musts*] (OIV, 1969).

2.2. Fermentation procedure

Fermentation of the juice, pws and paste substrates was carried out in 130 l vessels filled with 110 l of substrate. Three replications of all fermentations were performed. Temperature was regulated at 20 °C. The substrates were inoculated with a commercial yeast (*Saccharomyces cerevisiae* UCLM 325) up to a concentration of approximately 10^6 cells/ml. The process was monitored daily by measuring residual sugars, and the end of fermentation was determined on the basis of the sugar consumption (OIV, 1969).

Assimilable nitrogen was measured using the Nitro-Genius® kit.

In order to observe the influence of pH, in one series of fermentations, the pH was adjusted to around 4.0 with citric acid, which required the addition ca. 9 g/l of substrate and, in a second series, the substrates were fermented at their original pH (Table 1).

The alcoholic content was measured in each melon wine (OIV, 1969).

2.3. Distillation procedure

Upon completion of alcoholic fermentation, the wine made from the juice was immediately distilled in a tra-

ditional 130 l "*alquitara*", (reflux still) (Silva, Macedo, & Malcata, 2000) filled to 70–80% of capacity, equipped with a series of temperature sensors (Table 2). Distillation flow rate was set at 170 ml/min, and the condenser was kept below 21 °C throughout. The other melon wines, made from the pws and the paste, were pressed in a vertical pneumatic membrane press, and the resulting wine was then poured into the same 130 l reflux still under the same conditions. The distillate was collected in volumes of 1 l each, except for the head fraction. The first distillation was stopped when the alcohol content in the volume collected had reached 9.2–11.8 (v/v), which yielded a distillate with an alcohol content of 18.5–25% (v/v), depending on the source of substrate from which it had been made. The head-fraction (200 ml), usually discarded, was analysed and not rejected.

The second distillation was carried out in a traditional 30 l alembic still (Silva et al., 2000) filled with 15 l of the first distillate. Distillation flow rate was set at 35–40 ml/min. The heads, 0.8% of the distillate, were discarded, and distillation was stopped at 40% (v/v), thus yielding a final distillate (hearts) of 58–69% (v/v), again depending on the source substrate from which it had been made. The tails comprised the fractions from 40% to 5% (v/v). The alcohol content in the heads, hearts, and tails fractions, collected in volumes of 250 ml each, was measured by an aerometric method according to the European Union (2000). To prevent aroma loss, the fractions were collected on ice and kept at 4 °C until analysis. The final spirits were stored in 8 l glass demijohns at 4 °C, and the alcohol content was determined by electronic densimetry (European Union, 2000).

2.4. Analysis of the distillates

The major volatile compounds in the hearts fractions of all the distillate types and in commercial spirits (pears, cherries, and raspberries, along with Spanish *orujo* and Italian *grappa*) were analysed by GC (Hernández Gómez et al., 2003).

The rest of the volatiles of melon distillates were analysed by GC–MS on a Trace200 gas chromatograph equipped with an automatic AS2000 injector and con-

Table 1
Mean pH, °Brix, and alcohol contents % (v/v) for the different substrates tested and the resulting melon wines

	Substrate				Melon wines			
	pH		°Brix		Alcohol content % (v/v)			
					pH-unadjusted		pH-adjusted	
	X	SD	X	SD	X	SD	X	SD
Juice	6.0	0.1	9.9	0.1	3.3	0.3	3.5	0.7
pws	5.9	0.1	10.1	0.1	2.5	0.7	3.5	1.1
Paste	6.2	0.2	8.6	0.4	2.0	0.5	3.0	0.1

pws = Paste without skins, X = average, SD = standard deviation.

Table 2
Temperature, time and alcohol content values in a traditional reflux still during the first distillation of pws pH-adjusted melon distillate

Cut volume	Time	% v/v	T2	T3	T4	T5
Heads	1′ 30″	51	78	62	40	69
1	6′ 00″	39.5	80	70	53	75
2	5′ 30″	34.3	80	72	61	75
3	5′ 30″	31.6	80	73	66	76
4	5′ 40″	29.4	80	75	68	76
5	5′ 55″	27.0	81	75	69	76
6	5′ 45″	23.9	81	76	70	76
7	6′ 06″	21.1	81	76	71	76
8	6′ 08″	18.7	81	77	71	77
9	6′ 11″	16.3	81	77	71	77
10	6′ 17″	14.7	81	78	72	77
11	6′ 22″	12.8	81	78	72	77
12	6′ 22″	10.9	81	78	72	77
13	6′ 30″	9.5	82	79	72	77

$T2$: Temperature (°C) swan's neck, $T3$: temperature (°C) reflux column, $T4$: temperature (°C) column return, $T5$: temperature (°C) condenser coil, pws = paste without skins.

1. Boiler; 2. Swan's neck; 3. Reflux column; 4. Column return; 5. Condenser coil; 6. Distillate outlet
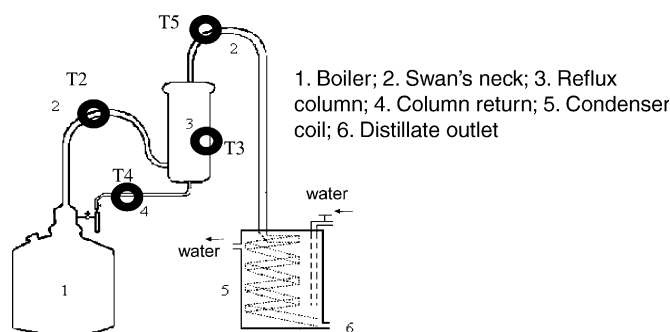
nected to a TraceMS mass spectrometer with an electron impact ionization source and quadrupole analyser from ThermoQuest. The chromatographic column used for the separation was a 50 m × 0.31 mm (i.d.) BP21 column (SGE, FFAP-type) coated with a stationary phase having a film thickness of 0.25 μm. The oven temperature programme was 43 °C (15 min isothermal) raised at 2 °C/min to 125 °C, at 1 °C/min to 150 °C, at 4 °C/min to 200 °C (45 min). Samples were injected using a split/splitless injector at 190 °C in splitless mode (splitless time: 0.5 min, split ratio: 27). The carrier gas was helium at a constant flow rate of 1.4 ml/min. The mass spectrometer was operated in electron impact mode at 70 eV, scanning the range of m/z 39–400. Transfer line temperature was 220 °C.

Identification of volatile compounds by GC–MS was achieved by comparison of the GC retention times and mass spectra with those of pure standard compounds. Quantitative results were obtained by the internal standard method based on the specific m/z ions of each compound.

2.5. Sensory evaluation

2.5.1. General conditions

Sensory evaluations were performed to select the best among the six distillates produced. All evaluations were carried out in a standardized tasting room (Spanish standard UNE 87004:1979) (AENOR, 1997) using standard wine-tasting glasses (Spanish standard 87022: 1992 and ISO standard 3591:1977) (AENOR, 1997) filled with 30 ml of distillate. Distillates were diluted with distilled water to an alcohol strength of 30% (v/v) and they were served at a temperature of 15 °C. Evaluations were held in the mornings between 10:00 a.m. and 12:00 noon.

2.5.2. Triangle test (Spanish standard UNE 87006:1992 and ISO standard 4120:1983) (AENOR, 1997)

This test was designed to ascertain the effect of fermentation substrate pH. The taste panel was composed of 18 tasters who were familiar with the product, and evaluations were performed on different days to avoid tiring. The distillates, at both pH levels, were tested in three different sessions: first, juice; second, pws and third, paste.

2.5.3. Preference test (Spanish standard UNE 87023:1995 – ISO standard 4121:1987) (AENOR, 1997)

Eighteen tasters familiar with the product took part. The distillate juice, pws, and paste at both pH levels were tested in two different sessions. Friedman's test and Fisher's significance tests were employed to establish the preference ranking. The paste distillate was rejected. The

same test was performed by the 18 tasters and 14 other tasters from a private spirit-manufacturing company for the juice and pws (both pH) distillates to establish the ranking.

2.6. Statistical analysis

Principal component analysis (PCA) was run on the different volatile compounds [esters, methanol, and aromatic higher alcohols (HAs), namely, 1-propanol, 2-methyl-1-propanol (2M1P), 2-methyl-1-butanol (2M1B), 3-methyl-1-butanol (3M1B), 2-phenylethanol, 1-butanol, 1-hexanol, and *cis*-3-hexen-1-ol] using the SPSS statistical package (11.0 version).

Student's *t*-tests were applied to the above-mentioned volatiles to ascertain possible significant differences between the distillates as a consequence of pH.

3. Results and discussion

3.1. Fruit processing

Previous papers (Hernández Gómez et al., 2003) reported that the paste substrate was unsuitable for fermentation (sluggish fermentation, high methanol and ethyl lactate contents). Nevertheless, further testing was continued because this type of fruit processing resulted in high yields, and additionally because further sensory evaluation was needed.

Melon fruits were processed in the study season in the amounts of 1500 kg for juice, 768 kg for pws, and 903 kg for paste, affording yields of 60.0%, 79.0%, and 99.8% (w/w), respectively. Comparing these yields with those reported for the year before (Hernández Gómez et al., 2003), increases of 10% were recorded for the juice and pws substrates, perhaps due to optimization of procedures. By-product yields were 21% (w/w) of skins for the pws substrate and 40% (w/w) skins and pressed pulp for the juice substrate.

Table 1 lists the pH, °Brix, and alcohol content for the different substrates tested. °Brix and alcohol contents were lower than in previous harvests (Hernández

Gómez et al., 2003), because of delays in harvesting the fruits (October rather than August), thereby causing in poorer fruit quality.

3.2. Analysis of the fermented melon wines

Based on the °Brix, the theoretical alcohol production expected was around 4–5% (v/v), but the values obtained were lower (2.0% to 3.5% (v/v)), although the final reducing sugar content was zero. On the whole, the wines fermented from the pH-unadjusted fermentation substrates had lower alcohol contents than the ones from the pH-adjusted fermentation substrates, due probably to the presence of acetic acid bacteria in the former (Hernández Gómez et al., 2003).

3.3. Distillation process

Table 2 shows the temperatures in the different parts of the reflux still, during the first distillation, for the pH-adjusted pws substrate, the temperature values for the rest of the distillations being similar (data not shown). The heads began to elute at 78 °C in the swan's neck (T2) and 40 °C in the reflux column.

For all the distillates, the alcohol content of the last volume collected was between 9.2% and 11.8% (v/v), and the final alcohol content of the distillates was between 18.5% and 25% (v/v) (Table 3).

In the second distillation, performed in the alembic still, the heads (0.8% of the total spirit collected) were discarded, and the alcohol content decreased from 74.5% to 40.0% (v/v) in the last volume collected. The total distillation time for all the fractions was around 4 h.

In general, the alcohol content of the double-distilled melon spirit was between 58% and 69% (v/v) (Table 3), depending on the type of substrate used. The highest value was for the juice distillate (pH-adjusted) and the lowest for the paste (pH-unadjusted) distillate.

3.4. Evolution of major volatiles during second distillation

After the second distillation, the major volatiles present in the heads, hearts, and tails fractions of the

Table 3
Alcohol content % (v/v) in the distillates at the respective cut-off points in the first and second distillations and on completion of the first and second distillations

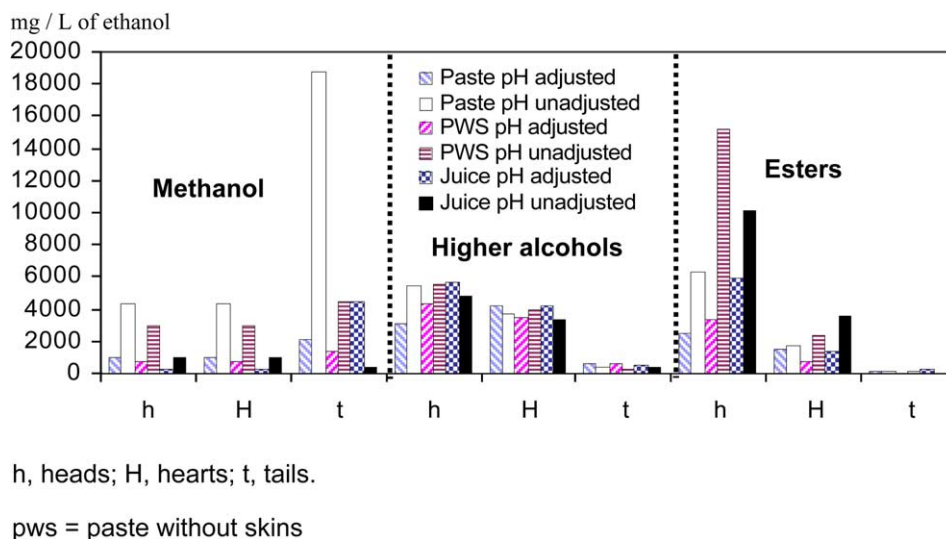|	First distillation cut-off	First distillate	Second distillation cut-off	Double-distilled spirit
pH-adjusted juice	11.7	25.0	41.0	69.0
pH-unadjusted juice	9.4	19.0	42.5	68.0
pH-adjusted pws	9.5	22.5	42.0	62.5
pH-unadjusted pws	9.2	19.5	40.0	60.0
pH-adjusted paste	10.6	18.5	40.0	61.0
pH-unadjusted paste	11.8	22.5	41.0	58.0

pws = Paste without skins.

Fig. 1. Evolution in major volatile compounds during the second distillation. Methanol. Higher alcohols: 2M1P, 2M1B, 3M1B, and 1-propanol. Esters: ethyl lactate, ethyl acetate, and ethyl butyrate (mg/l of EtOH). h, heads; H; hearts, t, tails; pws = paste without skins.

different spirits were analysed. The changes in the major volatiles content are depicted Fig. 1. Methanol was collected in nearly the same proportion in all the fractions, most likely due to the formation of azeotropic mixtures (Orriols, 1994). Nevertheless, methanol concentrations were higher in the distillates from the pH-unadjusted wines except for "juice" tails. High levels of methanol in the paste distillate were observed (pH-unadjusted).

The HA (2M1B, 3M1B, 1-propanol, and 2M1P) content was higher in the heads and hearts than in the tails. All the distillates displayed the same behaviour, with no marked differences among them. In addition, the HA content was not related to the fermentation pH or substrate types.

The ester (ethyl acetate, ethyl lactate, and ethyl butyrate) content was higher in the heads, decreasing in the hearts and the tails. Fermentation pH had a pronounced influence on the ester content.

3.5. Analysis of the distillates

3.5.1. Overall analysis

Table 4 presents the concentrations of the volatiles analysed in the final spirits.

3.5.2. Alcohols

3.5.2.1. Methanol. High amounts of methanol and 2-butanol can make spirits hazardous for consumers, health (Raposo, 1986). Moreover, methanol imparts a cooked cabbage odour, with a threshold of 1200 mg/l

(Ribéreau-Gayon et al., 2000). The methanol content was higher in the distillates made from the pH-unadjusted material in all substrates. The paste distillates exhibited the highest levels, probably owing to the action of certain pectinases on the substantial amount of melon skins present (Cortés Diéguez, Gil de la Peña, & Fernández Gómez, 2000; Ribéreau-Gayon et al., 2000). However, in no case did the levels exceed the limits for fruit spirits set by the legislation currently in force (European Union, 1989).

3.5.2.2. Higher alcohols. HAs, are responsible for imparting complex sensory attributes to spirits (Silva et al., 2000). The amyl alcohols (2M1B, 3M1B) and 2M1P contribute positively to the sensory characteristics (Bertrand, 1975; Orriols, 1992, 1994). They are detectable organoleptically at concentrations below 15 mg/l of ethanol (Tourliere, 1977). 1-Propanol has a pleasant, sweetish odour, but excessive concentrations will introduce solvent notes that mask all the positive notes in distillates (Fundira, Blom, Pretorius, & van Rensburg, 2002). The highest 1-propanol contents were recorded in the distillates made from the pH-adjusted fermentation substrates; in contrast, 2M1P was lower in the pH-adjusted distillates at levels similar to those reported in previous years. Amyl alcohol contents were very similar in all cases. 1-Butanol has a heavy, penetrating odour, and 2-butanol is associated with low-quality raw materials (Cortés Diéguez et al., 2000; Orriols & Bertrand, 1990). 1-Butanol concentrations were higher in the pH-adjusted distillates. Conversely, 2-butanol was not detected in any of the distillates produced. 2-Phenylethanol imparts a very clinging, rose-like aroma (Nykänen &

Table 4
Volatile compounds in the melon spirits (mg/l of ethanol)

Volatile component	Threshold (mg/40% v/v)	pH-unadjusted			pH-adjusted		
		Juice	Pws	Paste	Juice	Pws	Paste
Alcohols							
Ethanol % (v/v)		68.0	60.0	58.0	69.0	62.5	61.0
Methanol	1200[a]	975	2926	4316	306	681	958
1-Propanol		600	731	655	886	952	1065
2 Methyl-1-propanol		1013	10421	915	773	653	844
2-Methyl-1butanol		359	445	459	441	340	439
3-Methyl-1butanol		1348	1696	1678	2049	1501	1897
2-Phenylethanol		19	11.7	10.4	5.96	12.0	10.1
1-Butanol		8.41	10.6	9.25	16.5	20.4	21.0
2-Butanol		0.0	0.0	0.0	0.0	0.0	0.0
3-Methyl-3-buten-1-ol		1.54	1.52	1.83	1.25	1.08	1.35
3-Ethoxy-1-propanol		0.64	0.43	0.22	0.28	0.34	0.38
1-Hexanol	20[b]	1.03	1.20	1.79	0.37	0.51	0.97
cis-3-hexen-1-ol	3.5[c]	0.61	0.61	0.83	0.39	0.30	0.42
Benzyl alcohol	2–3[d]	2.67	2.22	2.22	0.27	0.69	1.91
* 3-Octanol		0.01	0.01	0.01	0.00	0.00	0.01
* 1-Octanol		0.04	0.03	0.03	0.11	0.05	0.06
* 1-Octen-3-ol		0.02	0.02	0.02	0.00	0.01	0.01
* t-3-Nonenol		0.20	0.14	0.18	0.11	0.08	0.09
* t-6-Nonenol		0.31	0.14	0.22	0.18	0.07	0.09
* 3,6-Nonadien-1-ol		0.72	0.42	0.53	0.45	0.30	0.31
4-Methyl-guaiacol		8.07	11.4	13.4	0.01	2.16	3.67
Syringol		0.05	0.04	0.02	0.04	0.03	0.04
Geraniol	0.096[e]	0.18	0.18	0.18	0.03	0.04	0.03
Total alcohols		4339	6881	8065	4481	4163	5243
Total alcohols–methanol		3364	3954.4	3749	4175	3483	4285
Aldehydes							
Acetaldehyde		278	340	204	271	391	575
Furfural		2.60	4.14	3.26	1.36	0.97	1.25
3-Hydroxy-2-butanone		1.42	2.51	1.50	1.27	70.4	18.2
Benzaldehyde		0.40	0.65	0.54	0.47	0.37	0.68
* Damascenone		0.09	0.09	0.16	0.09	0.08	0.12
Vanillin		0.05	0.08	0.02	0.15	0.03	0.06
Total aldehydes		283	347	210	275	463	595
T. aldehydes-acetaldehyde		4.7	7.6	5.8	3.5	72.0	20.6
Esters							
Ethyl acetate	200–1200[f]	3260	1712	1391	1242	479	985
Ethyl lactate		365	642	372	158	268	402
Ethyl butyrate		0.0	9.1	24.5	0.0	0.0	36.1
Ethyl caproate		1.42	1.04	0.79	5.81	2.68	4.73
Ethyl caprilate		4.65	4.51	3.10	31.8	9.37	16.4
* 2-Hydroxyethyl caproate		0.27	0.26	0.19	0.05	0.05	0.07
* Ethyl decanoate		2.50	3.48	2.06	24.8	11.4	9.85
* Ethyl laurate		0.60	1.27	0.69	4.00	4.21	1.23
* Ethyl stearate		0.02	0.04	0.03	0.04	0.05	0.02
Ethyl palmitate		5.86	12.3	6.55	11.0	17.9	5.85
* Ethyl linoleate		0.11	0.26	0.17	0.16	0.18	0.09
* Ethyl myristate		0.14	0.37	0.18	0.66	0.74	0.24
* Ethyl 9-hexadecenoate		0.05	0.07	0.06	0.09	0.07	0.03
* Ethyl 9-octadecenoate		0.01	0.02	0.01	0.02	0.03	0.01
2-Phenylethyl acetate		2.65	1.29	2.10	1.77	4.89	2.61
* Benzyl acetate		0.03	0.03	0.03	0.02	0.03	0.02
Isoamyl decanoate		0.12	0.40	0.15	2.10	1.34	0.50
* 2,3-Butanediol diacetate		0.03	0.04	0.03	0.04	0.02	0.05
Total esters		3651	2400	1810	1543	833	1488
Total esters – e.acetate		381	673	411	221	310	472
T.esters-(e.acet. + e.lact.)		16.2	31.0	38.6	63.1	42.4	70.3
Carboxylic acids							
Decanoic acid	8[g]	22.3	31.6	16.4	51.9	52.3	53.8

Table 4 (*continued*)

Volatile component	Threshold (mg/40% v/v)	pH-unadjusted			pH-adjusted		
		Juice	Pws	Paste	Juice	Pws	Paste
Octanoic acid	15[g]	13.5	14	9.92	26.1	21.9	38.9
Isobutyric acid	1.4E − 5[g]	2.87	3.93	3.70	3.20	2.90	3.57
Hexanoic acid		1.58	1.79	0.63	3.65	3.09	5.01
Isovaleric acid		0.64	1.61	1.14	1.09	0.79	0.90
* 2-Methylbutanoic acid		0.07	0.11	0.11	0.08	0.07	0.09
* Lauric acid		0.21	0.71	0.13	0.49	0.43	0.38
* Hexadecanoic acid		0.07	0.00	0.00	0.04	0.02	0.08
* Dihydroxycinnamic acid		0.02	0.02	0.02	0.02	0.02	0.02
* Myristic acid		0.04	0.09	0.02	0.06	0.02	0.06
Total carboxylic acids		42.2	55.7	32.6	87.9	82.6	104.1
Others							
* Trimethyl-tetrahydro-naphthalene		0.04	0.04	0.05	0.16	0.08	0.10
* 1,1,3-triethoxy-propanol		0.13	0.14	0.13	0.02	0.03	0.04

* Compounds quantified from the specific m/z ions using the internal standard method.

T. = total.

e.acet. = ethyl acetate.

e.lact. = ethyl lactate.

[a] Ribéreau-Gayon, Glories, Maujean, and Dubordieu (2000).

[b] Tourliere (1977).

[c] Jouret and Cantagrel (2000).

[d] Blaise (1986).

[e] Rogerson and De Freitas (2002).

[f] Cortés, Gil, and Fernandez (2002).

[g] Soufleros (1978).

Suomalainen, 1983), and was not influenced by pH, except in the juice distillates.

1-Hexanol, cis-3-hexen-1-ol, and 3-methyl-3-buten-1-ol impart strong herbaceous aromas. Hexanol and cis-3-hexen-1-ol perception thresholds in spirits are 20 and 3.5 mg/l, respectively (Jouret & Cantagrel, 2000), and the concentrations did not exceed those values. Smoked or burnt wood aroma is conferred by 4-methyl-guaiacol (Dubois & Dekimpe, 1982), and it was present in all distillates except the pH-adjusted juice.

Benzyl alcohol is related to the quantity of benzaldehyde, the latter being important because it imparts a bitter almond aroma to wines at levels above 2–3 mg/l (Blaise, 1986). In the present study, concentrations were nowhere near that perception threshold.

3.5.3. Aldehydes

3.5.3.1. Acetaldehyde. Acetaldehyde constitutes 90% of the total aldehyde content (Orriols, 1991, Silva, Malcata, & Hogg, 1995; Versini, Monetti, dalla Serra, & Inama, 1990). More than 1200 mg/l of ethanol is evidence of oxidation of the ethanol during alcoholic fermentation or a enzymatic pyruvic acid decarboxylation (Baro & Quiros-Carrasco, 1977; Cantagrel, Lablanquie, Snakker, & Vidal, 1993). Its importance derives from its pungent odour and its chemical reactivity (Silva et al., 2000). pH had no effect in juice and pws substrates; in contrast, it was doubled in pH-adjusted paste distillate. Furfural may be formed as a result of oxidation of ascorbic acid (Bayodove, Baumes, Crouzet, & Günata, 2000). A slightly higher furfural content in the distillates from the pH-unadjusted substrates was observed.

3.5.4. Esters

Esters are associated with pleasant odours. This is particularly true of ethyl acetate, which contributes to aroma complexity and has a positive impact at very low levels (50–80 mg/l) (Steger & Lambrechts, 2000). Ethyl acetate was higher in the pH-unadjusted distillates. Ethyl lactate contributes intense, long-lasting aromas (Tourliere, 1977). The content in distillates is linked to lactic fermentation, in general it was lower in pH-adjusted distillates (Briones et al., 2002).

Ethyl butyrate adversely influence the organoleptic quality of distillates (Soufleros, 1978, 1987). Paste distillates, at both pH levels had the highest concentrations.

Concentrations of the minor esters, other than ethyl lactate and ethyl acetate, were higher in the pH-adjusted distillates, due principally to ethyl caprylate, ethyl palmitate, ethyl caproate, ethyl laurate and ethyl decanoate.

3.5.5. Carboxylic acids

Short-chain (C_4–C_{12}) fatty acids produce unpleasant odours, and high concentrations are an indicator of poor quality (Orriols, 1992, 1994). Decanoic and octanoic acids were the most abundant fatty acids and were present at higher concentrations in the pH-adjusted distillates.

3.6. Comparison with commercial spirits

The major volatile compounds of pH-adjusted juice and pws distillates were compared with other commercial spirits and the results are depicted in Fig. 2.

In general, 1-propanol was higher in melon distillates, being similar to concentrations in *grappa* and cherry spirit. In like fashion, ethyl acetate was much higher in the juice distillate with a concentration nearly thrice those of other spirits. Acetaldehyde and ethyl lactate were present in similar amounts in most of the spirits considered, with the exception of much higher concentration of ethyl lactate found out in the cherry spirit, most probably as a result of the lengthy maceration time. 2M1P, 2M1B, and 3M1B were somewhat higher in the melon distillates, pear spirit, and *grappa*. The melon distillates had appreciably lower methanol contents (see Table 4) than the rest of the spirits considered, particularly as compared to the pear spirit (11216 mg/l of ethanol), most likely because of the high pectin content of pears.

1-Butanol was detectable in the pear spirit and, to a lesser extent, in the melon distillates. 2-Butanol and ethyl butyrate were not present in detectable amounts in any of the spirits analysed.

3.7. Statistical analysis

PCA of the volatile compounds listed in Table 4, was run to determine the distribution of the samples in the plane. Principal component 1 (PC1) and principal component 2 (PC2) explained 70% of the variance. Table 5 shows the volatiles that best correlated with the two principal components, the variance explained by each compound and their contribution to the corresponding principal component. Fig. 3 plots the samples on a plane defined by PC1 and PC2, which best explain the variance between samples and shows that those from pH-unadjusted substrates were clustered together. Ethyl decanoate, ethyl caproate, and ethyl caprylate were the volatiles that contributed best to PC1. Concentrations of all three of these compounds were lower in the distillates from the pH-unadjusted substrates. On the other hand, distillates from the pH-adjusted substrates were clearly separate for the two principal components.

When a Student's *t*-test ($\alpha = 0.05$) was applied to the volatile compounds produced at both pH levels, 1-propanol, 1-butanol, 1-hexanol, 2-OH-ethyl

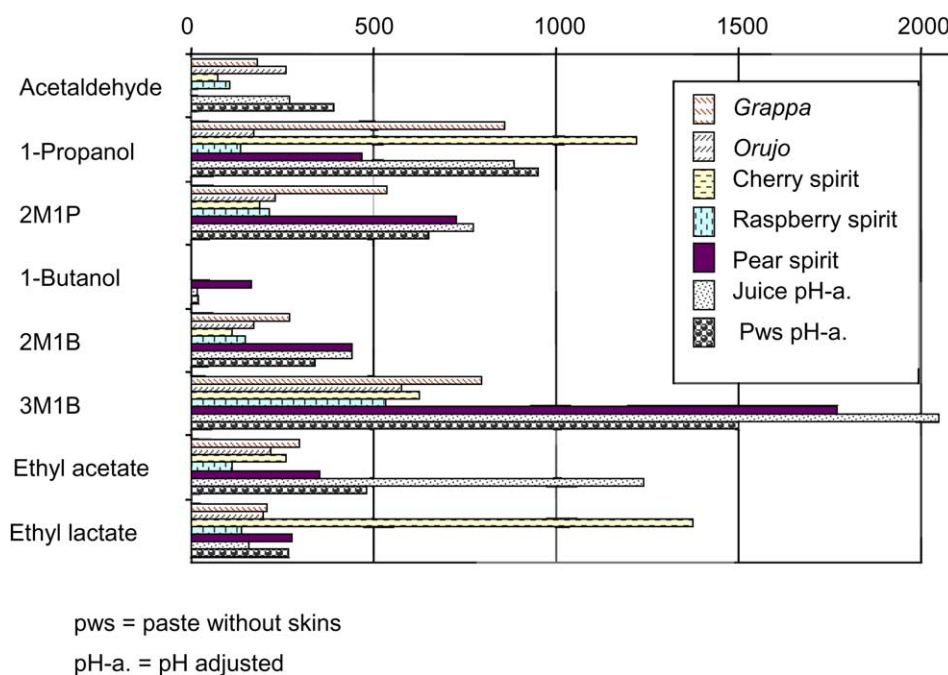pws = paste without skins

pH-a. = pH adjusted

Fig. 2. Comparison of some volatile compounds (mg/l of EtOH) in juice and pws pH adjusted distillates with grappa, orujo, cherry spirit, raspberry spirit, and pear spirit. pws = paste without skins; pH-a. = pH adjusted.

Table 5
Factor loadings and variance explained by the first two principal components obtained by PCA analysis of the volatile compounds of melon spirits

| Principal component	Variance explained (%)	Total variance (%)	Variable highly correlated and their loadings
PC1	45.43	45.43	Ethyl decanoate (0.945)
			Ethyl caproate (0.940)
			Ethyl caprylate (0.920)
			2-Hydroxyethyl caproate (−0.909)
			Isoamyl decanoate (0.885)
			Benzyl acetate (−0.871)
			1-Propanol (0.813)
			1-Butanol (0.812)
PC2	24.67	70.10	Ethyl palmitate (0.859)
			Ethyl 9-octadecenoate (0.791)
			2,3-Butanediol diacetate (0.779)
			2-Methyl-1-butanol (0.765)
			Ethyl stearate (0.750)
			Ethyl butyrate (0.723)
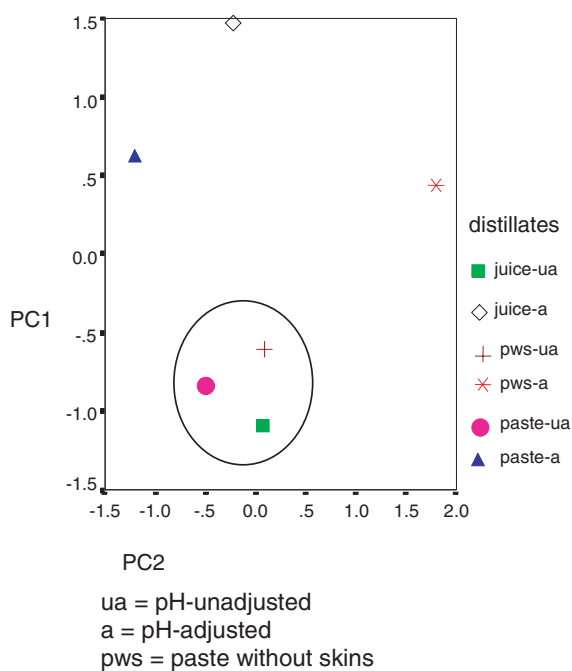
Fig. 3. PCA analysis of the volatile compounds of differents melon spirits. ua = pH unadjusted; a = pH adjusted; pws = paste without skins.

caproate, and cis-3-hexenol showed significant differences.

3.8. Sensory analysis

To study the effect of fermentation pH, a sensory analysis (Section 2.5) was applied and results are shown in Fig. 4. According to the triangle-test (see Section 2.5.2), there were significant differences between juice distillates (at the 95% level) and pws (at the 99% level).

Conversely, there were no significant differences between the paste distillates.

To study the effect of different substrates, a sensory analysis was carried out (Section 2.5.3). The results of the preference test, performed in the first session on the three distillates made from the pH-unadjusted substrates (Fig. 4) were as follows: between paste and pws distillates, tasters preferred the latter (95% confidence level) and between paste and juice, again the latter (99% confidence level). Finally the analysis shows no preference between juice and pws.

The second preference test applied to pH-adjusted distillates showed differences between paste and juice, the latter being preferred (95% confidence level) and between paste and pws, again also the latter being preferred at the same level. There were preferences between pws and juice distillates.

An additional preference test on the distillates from juice and pws, at the different pH levels, showed no preferences at the 95% confidence level. The expert tasters from a distilling company likewise expressed no preferences, possibly because the spirits being tested were new to them and had an unfamiliar flavour.

3.9. Relationship between volatile compounds and sensory analysis

Distillate quality depends on the contents of such compounds as methanol, acrolein, allyl alcohol, diacetyl, ethyl acetate, ethyl lactate, diethyl succinate, 1-propanol, 1-butanol, and 2-butanol (Silva et al., 2000). Contamination of the raw materials and improper fermentation are the sources of most of these compounds. In this study, some of these compounds (methanol, ethyl acetate, ethyl lactate and 1-butanol)
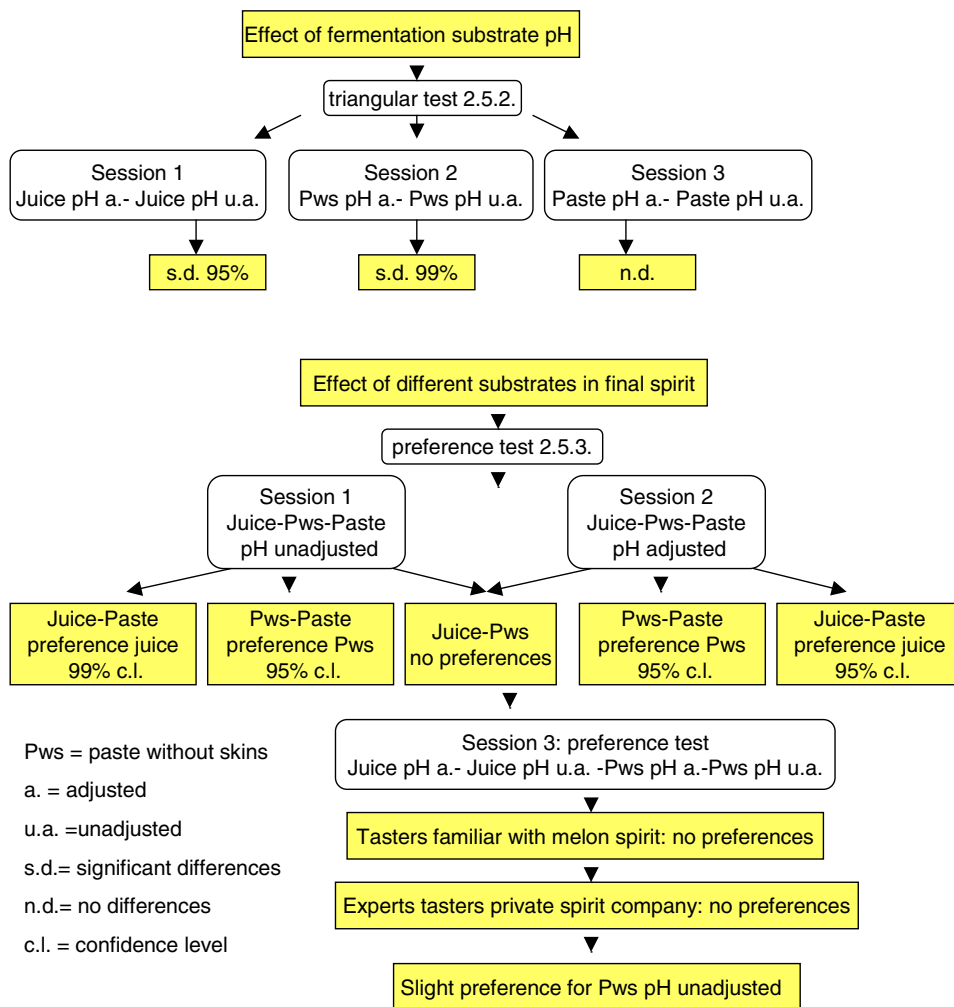
Fig. 4. Sensory evaluations of melon sprits.

were lower in pH-adjusted substrates than in the pH-unadjusted ones.

PCA grouped the distillates according to substrate pH, which corroborated the triangle test results for the pws and juice distillates (Fig. 3). Student's *t*-test also substantiated the triangle test results, again finding significant differences according to fermentation substrate pH.

4. Conclusions

The paste distillates were given negative ratings. The fermentation pH brought about perceptible differences based on both the chemical and the sensory analysis. Nevertheless, the tasters expressed no preference between pws and juice according to fermentation pH.

From an industrial standpoint, the pws substrate can be regarded as preferable, because it produces less waste with a lower environmental impact and it is not necessary to press the paste to obtain it.

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