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Influence of ripening stage on volatiles composition, physicochemical indexes and sensory evaluation in two varieties of muskmelon (*Cucumis melo* L var *reticulatus* Naud)

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Abstract: The quality parameters of muskmelon (*Cucumis melo* L var *reticulatus* Naud) are often related to sugar content and aroma composition. A study of aroma composition using two different extraction techniques (GC-HS and GC-MS extraction concentration) was performed in order to find correlations with sensory descriptors, other quality indices and ripening stage. Two muskmelon varieties (Calypso and Pamir) were assayed at three different ripening stages (unripe, ripe, overripe). Chemical, physical and sensory analyses were performed on the muskmelon samples just after harvest and after 7 days of cold storage. Solid soluble content (SSC) changed from about 10 °Bx in unripe samples to about 15 °Bx in ripe and overripe samples. Different aroma composition and sensory evaluation were found depending on the ripening stages. The main flavour components detected were esters which increased 10–15-fold from unripe to ripe and overripe stages. The acceptance judgements by panellists were strongly correlated with the sensory descriptor flavour. High statistical correlations were also found between sensory descriptor flavour and some classes of aroma compounds, mainly with total esters (about 0.66–0.69), formates (0.70) and acetates (0.64 and 0.72). The paper demonstrates that some classes of esters are very important to assess the sensory flavour and overall eating quality of muskmelons.

Keywords: muskmelon; sensory analysis; aroma composition; quality parameters

INTRODUCTION

Understanding which physicochemical parameters are strongly associated with consumer preference and acceptance will permit identification of both high-quality fruit and optimal harvest time. This would assist melon growers in harvesting fruit with high market quality.

High soluble solids concentration (SSC) at harvest does not always correspond to high overall fruit quality and should be used in conjunction with the evaluation of flavour.[1] On the other hand, measurement of SSC with a refractometer is quick and easy but it is destructive and requires a large sample size to be reliable, while flavour evaluation, which can be performed by both chemical methods and sensory analysis, is time-consuming and requires a sensory panel.

Sugar concentrations depend on ripening stage, which is also associated with increased respiration and ethylene production rates, softening and aroma development.[2] As postharvest changes in sugar concentrations are small, harvesting at the appropriate stage of maturity is crucial to good eating quality.[1–3] Good eating quality also implies good aroma; volatile composition is also related to fruit maturation.[4]

More than 160 compounds have been identified in the volatile fraction of muskmelon.[5] The flavour of melons is due to a complex but well defined mixture of different classes of compounds,[6] but two groups stand out as a characteristic feature of the volatile composition of melon fruits: C_9 compounds (saturated and unsaturated aldehydes and alcohols) and some volatile esters which are the most responsible for the melon-like and fruity notes, respectively.[7,8] However the techniques employed to obtain the aroma samples are responsible for the striking differences between the results reported by different research groups. Moreover, several factors, such as ethylene, fruit maturity and attachment to the parent plant, influence the production of volatiles by muskmelons during the ripening period.[6]

Aroma volatile compounds are responsible for aroma, but the sensory quality of melons and the overall acceptance by consumers depend on the

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combination of aroma, taste and texture. It is not an easy task to investigate how the melon composition influences the sensory descriptors.

The volatile composition, however could be affected by storage conditions after harvesting, although Kemp *et al*[9] did not show marked differences in volatile composition in melons refrigerated for 2 weeks compared with freshly harvested melons. Yet little is known about the modifications during refrigerated storage of melons harvested at different ripening stage.

In a previous work on muskmelon[10] a high correlation was found between the descriptors acceptance and aroma and between the descriptors acceptance and sweetness. As regards aroma composition, ethyl esters (excluding ethyl acetates) were reported as very important compounds for the melon flavour and could be considered as an index of a good quality aroma. Therefore, the amount of these esters could be considered as a marker of a good quality melon aroma. The headspace technique used for the cited previous work did not detect the C_9 and other high-boiling compounds.

Different extraction techniques should be used in the study of aroma compounds because they strongly influence the spectra of volatile compounds.[6] Therefore the headspace technique[10] was combined with the extraction–concentration technique[11] in order to obtain a wider spectrum of volatile compounds.

The objectives of this research were: (1) to evaluate some chemical indexes and aroma compounds in relation to the ripening stage which depends on the harvest time; (2) to find the correlation between aroma compounds and sensory evaluation; and (3) to check the changes occurring after chilled storage for 7 days.

MATERIALS AND METHODS

Raw material

Two commercial varieties of muskmelon (*Cucumis melo* L var reticulatus Naud) were tested: Calypso (segmented smooth-skinned) and Pamir (netted), both belonging to the orange-fleshed type and cultivated in a specialized area in the Emilia-Romagna region, Italy. Harvesting was carried out in July. Fruits were picked by hand at three different ripening stages checked according to the practical experience of the specialized muskmelon growers: (1) optimum commercial maturity stage (= ripe); (2) 2 days before optimum commercial maturity stage (= unripe); and (3) 2 days after optimum commercial maturity stage (= overripe).

Immediately after harvesting the fruits were put in a cold box and conveyed to the laboratory, where six fruits for each variety and every ripening stage were selected on a random basis and kept cool at $2 \pm 1\,^{\circ}C$ (RH 90%). The physical (texture, colour), chemical (soluble solids content, titratable acidity, total sugars, aroma compounds) and sensory analyses were performed 24 h after the arrival at the laboratory (T_0) and after 7 days of cooled storage (T_7).

Physical analyses

Colour measurements were performed with a reflectance colorimeter Minolta Chromameter CR 200 (Minolta Co, Osaka, Japan), measuring the central part of the surface of both halves of six melons, randomly picked. The cutting was made blossom end to stem end and through the groundspot. Colour data were obtained by selecting C as colour space, and converting it into L^*, a^* and b^* values. From these values, hue (arctan b^*/a^* expressed as degrees) and saturation $(a^{*^2} + b^{*^2})^{1/2}$ were calculated.

The firmness of the melon fruits was determined with a dynamometer, Instron model 4301 (Instron Corporation, Canton, MA, USA) by measuring the maximum force (kg) required to press an 8 mm diameter probe into the pulp of 12 whole halves to a depth of 8 mm at a speed of $0.2\,m\,min^{-1}$.

Chemical analyses

A cylindrical portion of melon flesh was extracted with an appropriate tool from the central part of each fruit. The cylinder of melon flesh represented the transverse section of a fruit from the placenta cavity to epidermis.

A 15 mm length and 10 mm diameter cylinder was cut from the middle of the melon flesh cylinder and squeezed to measure in quadruplicate the soluble solids content (SSC) with a BS model RFM 81 refractometer (Tumbridge Wells, Kent, UK).

About 100 g of flesh were taken from the melon halves, homogenized and used for the determination of titratable acidity, total sugars and aroma compounds. Titratable acidity was determined in quadruplicate according to AOAC methods.[12] Sugars (sucrose, glucose, fructose) were determined in triplicate from an aqueous extract of the homogenized pulp (10 g to 100 ml), filtered on 0.45 μm filters and checked using HPLC (Jasco (Tokyo, Japan) 880 PU) at 85 °C, with water as mobile phase ($0.6\,ml\,min^{-1}$) on an Aminex HPX 87-C column (Aminex Biorad Laboratories, Hercules, Canada), with a refractometer as detector (Jasco RI 930). Total sugars were obtained by summing the amounts of single sugars.

The samples for aroma analyses were immediately frozen with liquid nitrogen and kept at −80 °C until use. The samples for headspace analysis (10 g) were frozen in a tightly closed vial of 20 ml volume.

Ethylene analysis

For the ethylene analysis, a sample of air was drawn with a gas-tight syringe directly from the internal cavity of each melon fruit kept for 24 h at room temperature and then assayed by GC-FID, with a gas chromatograph (DANI, model 3800) (Dani, Cologno Monzese (Milano), Itlay) equipped with a 1.5 ml loop injection valve, a 2 m stainless steel Alumina F1 (80–100 mesh) column held at 100 °C, and a flame ionization detector (FID) at 250 °C. Data were expressed as $\mu g\,g^{-1}$, after calibration with a standard at known concentration.

Aroma analysis

The extraction and characterisation of the aroma compounds were carried out by means of both static headspace GC analysis (HS-GC) and extraction–concentration of the aroma compounds by a coupled technique microwave (MW)-resin.[11] The volatile extracts were qualitatively and quantitatively analysed by GC/MS.

At the time of HS-GC analysis the vials with samples were kept at 80 °C for 60 min, then 500 µl of the head space gas were injected inter a GC analyser (DANI model 3800) by means of an automatic sampler (DANI 3950 HSS). Each variety was checked in quadruplicate.

The GC analyser was equipped with a wide-bore DB-WAX column (length = 60 m; internal diameter 0.53 mm; film thickness 1 µm) and FID, with a He flux of 1.2 ml min^{-1}. The column temperature was programmed as follows: 50 °C for 10 min, then 3 °C min^{-1} up to 180 °C, then 10 min at 180 °C. The split ratio was 1:10, the injector port was at 230 °C, and the FID was at 250 °C.

The chromatographic peaks were identified and quantified using a known concentration of standard, dissolved in a 100 g kg^{-1} sugar solution and analysed in the same conditions as the samples. In order to validate the identification of the peaks, a known amount of commercial standard was added to the melon pulp and analysed like the other samples. In the extraction–concentration technique 300 g of each sample were dispersed into 300 ml of distilled water in a 1 l glass container equipped with two small tubes. One tube was connected with a N_2 cylinder while the other led to a glass column packed with 30 ml of KS112 apolar resin. The glass container was placed in a microwave oven (CEM, Orio al Serio (BG), Italy) operating at 440 W for 40 min. The volatile compounds generated were continuously removed from the glass container by means of a nitrogen flux and adsorbed on the resin.

The volatile extracts were recovered by eluting the aroma compounds from the resin with 100 ml of ethyl ether, which was then dried with anhydrous Na_2SO_4 and removed in a Kuderna-Danish evaporator (Supelco–Sigma Aldrich, St Louis, MO, USA).

The qualitative analysis was performed by injecting 0.5 µl of the volatile extracts into a DB-1 capillary column (length = 60 m; internal diameter = 0.25 mm; film thickness = 0.25 µm). The column temperature was programmed as follows: 50 °C for 5 min, then 2 °C min^{-1} up to 240 °C, then 20 min at 240 °C. The He flux was 2 ml min^{-1} and split 20 ml min^{-1}, while the temperature of the transfer-line was 240 °C. The MS spectra were generated at 70 eV and the 10–400 Amu mass range was selected.

The quantitative analysis was carried out using commercial standards. Known amounts of the various compounds were diluted and added to 300 g of melon pulp previously deflavoured and then analysed like the other samples.

Sensory analysis

Sensory analysis was carried out by a trained panel of 11 members (six females, five males, 25–50 years old) using a descriptive test with scaling.[13] Randomly coded samples were scored for firmness, sweetness, flavour, juiciness and acceptance using an interval scale of 125 mm with anchor points (little, very) at each end. The samples were randomly offered to the tasters and the sensory analysis was repeated the following day.

The figures are the distance of the judges' marks from the left end of the scale and represent the intensity of the sensory descriptor examined.

Statistical analysis

The data obtained from chemical and sensory analyses were submitted to analysis of variance and the averages were compared by Tukey multiple range test ($p < 0.05$). Correlation analysis was carried out between the sensory descriptors (acceptance, sweetness and flavour) and gas-chromatographic aroma parameters based on the averages of varieties. The volatile compounds submitted to correlation analysis were chosen according to their more abundant presence. A Statgraphics software package was used.[14]

RESULTS AND DISCUSSION

Influence of ripening stage

The ripening stage of fruits caused noticeable differences in most of the parameters investigated. However, the changes were much more evident if the ripe fruits were compared with the unripe ones than if the ripe fruits were compared with the overripe ones. The evidence concerns mainly SSC, acidity and dry matter (Table 1).

Ethylene content of the fruits showed a peak value (about 60 µg g^{-1}) at the ripe stage in both varieties. This confirms that the ripe fruits were picked at the right time, ie just at the maximum value of ethylene production. The ethylene peak value characterizes climacteric fruits[15] and accompanies the biochemical changes that lead to a good eating quality.[16]

One of the few differences noted in overripe fruits with respect to ripe ones is the colour parameters. The overripe melons of the Calypso variety showed significant differences with respect to the unripe and ripe fruits: brightness (L^*) decreased as well as hue and saturation. The Pamir variety behaved slightly differently: brightness decreased even at the ripe stage, while hue and saturation increased when ripe and overripe (Table 1).

The total sugars content measured by HPLC (Table 1) was in good agreement with the SSC determined by refractometer. However, a particular behaviour can be noted if the single sugars are looked for. In both varieties sucrose value rose from the unripe

Table 1. Chemical and physical analyses of the two melon cultivars at three different ripening stages after harvest (T_0) and after 7 days of cold storage (T_7)

	Calypso T_0			Calypso T_7			Pamir T_0			Pamir T_7		
Ripening stage	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe
pH	6.72aA	6.81aA	6.70aA	6.76bA	6.95aB	6.88bAB	6.16aA	6.63aB	6.40aAB	6.30aA	6.99bC	6.71bB
Acidity (meq kg^{-1} fw)	14.7aB	15.8bB	14.4bA	16.0bC	13.7aA	11.2aB	20.6cA	21.9aA	19.6bA	21.1cC	13.9cA	15.5cB
SSC (°Bx)	11.41bA	14.46bC	13.73aB	11.15aA	13.81aB	13.81aB	8.55bA	15.60aB	15.54aB	7.53aA	15.51aB	15.41aB
Dry matter (g kg^{-1})	117.4aA	146.4bC	136.7aB	110.4aA	137.2aB	137.2aB	92.1aA	157.6bC	153.6bB	91.0aA	152.2aB	150.7aB
Firmness (kg)	4.0aC	1.6aB	0.9aA	2.8bB	1.5aA	1.1aA	3.7aB	1.3aA	1.3aA	3.7aB	1.1aA	1.5aA
L^*	68.10aB	64.09aB	58.53aA	67.14aB	64.23aA	63.80bA	71.79aC	61.37bB	56.09aA	70.95aC	57.33aA	61.95bB
Hue (arc tan b^*/a^*)	68.69bB	68.69bB	73.82bA	74.39aA	74.89aA	75.65aA	86.57aA	75.43bB	74.89bB	80.35bA	77.05aB	76.50aB
Saturation	41.47bB	41.80bB	35.38aA	36.52aA	38.49aA	36.33aA	26.91aA	34.33bB	33.89aB	25.29aA	31.07aB	33.97aC
HPLC analyses												
Sucrose (g kg^{-1} fw)	34.3aA	80.4aC	73.7aB	62.3bA	89.6bB	85.0bB	10.4bA	100.8aB	87.9aB	4.7aA	96.0aB	75.5aB
Glucose (g kg^{-1} fw)	19.9aB	17.3bB	10.5aA	16.5aA	13.9aA	11.1aA	26.3aC	17.5aB	12.4aA	24.0aC	17.7aB	6.9aA
Fructose (g kg^{-1} fw)	19.1aC	15.4aB	12.4aA	19.3aB	14.8aA	14.3bA	25.9aC	19.1aB	15.0bA	25.7aB	17.7aB	7.9aA
Total sugars (g kg^{-1} fw)	73.3aA	113.1aB	96.6aB	98.1bA	118.3bB	110.4bB	62.6aA	137.4aC	115.3bB	54.4aA	131.4aB	90.3aAB

Mean values of three replicates for each sample.
Different letters mean statistically significative difference between times of storage ($p < 0.05$).
Different capital letters mean statistically significant difference between ripening stages ($p < 0.05$).

Table 2. Sensory analysis ratings of the two melon cultivars at three different ripening stages after harvest (T_0) and after 7 days of cold storage (T_7)

	Calypso T_0			Calypso T_7			Pamir T_0			Pamir T_7		
Ripening stage	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe
Sweetness	3.37aA	6.68aB	6.85aB	5.40bA	6.65aA	6.73aA	2.98aA	6.73aB	6.44aB	2.67aA	6.49aB	6.25aB
Flavour	3.05aA	5.76aB	6.93aB	4.03aA	6.23aB	7.61aB	2.41aA	5.98aB	5.98aB	2.82aA	6.03aB	5.89aB
Firmness	8.37aB	5.66aA	5.45aA	7.39aB	6.23aAB	5.15aA	9.33aB	5.47aA	5.42aA	8.57aB	3.93aA	5.56aA
Juiciness	4.00aA	6.89aB	7.77aB	4.71aA	7.53aB	7.34aB	2.55aA	6.30aB	7.78aB	3.04aA	7.13aB	7.24aB
Acceptance	3.04aA	5.76aB	7.29aB	4.09aA	6.53aB	7.38aB	2.19aA	6.23aB	6.25aB	2.25aA	5.65aB	5.56aB

Mean values of two replicates for 11 panellists.
Different letters mean statistically significant difference between times of storage ($p < 0.05$).
Different capital letters mean statistically significant difference between ripening stages ($p < 0.05$).

stage to the ripe stage and then remained at a high level, while glucose and fructose had their top value at the unripe stage. Therefore, it could be hypothesized that there is sucrose biosynthesis and accumulation during the ripening, due to the peculiar enzymatic pattern of muskmelon, as already shown by Hubbard *et al*[17] and Wang *et al*.[18]

There was a significant difference in the sensory descriptors between fruits harvested at ripe and overripe stage and those picked at the unripe stage (Table 2). In both varieties all the sensory descriptors reached the maximum value at the ripe and overripe stage, particularly acceptance and flavour, with the exception of firmness, which decreased as ripening continued; this was confirmed by the instrumental measure of firmness by dynamometer (Table 1).

The aroma evaluation was performed using two different techniques: GC-HS analysis of pulp and GC-MS total extraction–concentration. There were more significant differences in the aroma compounds found in the unripe samples than in ripe and overripe melons; this is reported in Tables 3 and 4. The differences were noted both in the type and in the quantity of the detected compounds. The unripe samples of both varieties had a very low amount of aroma compounds but, as the fruits ripened, there were some noticeable increases in the amounts of detected compounds. They were grouped in five and seven classes of compounds, respectively, for GC-HS data and extraction–concentration GC-MS (Figs 1 and 2). These classes differed mainly for the presence of formates in the headspace data and the presence of carbonyl compounds as well as sulphur compounds in the extraction concentration GC-MS data.

The total alcohols contents of the GC-HS samples stood out, due to the very high levels of ethanol and/or methanol (Table 3).

In GC-HS extracts the main representative compounds were the esters (Figs 1 and 2). The two varieties had slightly different patterns at T_0. The esters of Calypso did not markedly increase from ripe to overripe stage, while in Pamir esters increased noticeably at the overripe stage.

In extraction–concentration GC-MS samples, the differences between the varieties were less evident. In ripe fruits the amounts of total esters and total alcohols were almost at the same level, while the overripe fruits showed a predominance of total esters (Figs 1 and 2).

It should be noted that the most interesting single compounds for the fruity note of aroma were the esters 2-methyl-1-butyl formate and 2-methyl-1-butyl acetate for the GC-HS extracts (Table 3) and ethyl butanoate, 2-methyl-1-butyl acetate and hexyl acetate for the extraction–concentration GC-MS samples (Table 4).

A general consideration concerns the fact that the low amounts detected in unripe samples had a tendency to increase in ripe and overripe samples. Among the most abundant compounds were ethanol for GC-HS and acetoin for GC-MS extraction concentration, which are considered to be markers of fermentation metabolism. Ethanol and acetoin showed different behaviour depending on the variety. In fact, overripe fruits of Calypso show an increase of ethanol at T_7 (about 40 mg g^{-1} fresh weight, fw) and acetoin at T_0 (16 μg g^{-1} fw). This could mean that the Calypso variety is less suitable for delayed harvesting. Saturated and insaturated C_9 aldehydes and alcohols, which are considered to be the principal contributors to the typical green note of the muskmelon flavour,[9] were not found in either of the varieties, with the exception of the unripe fruits of cv Pamir. This lack of the C_9 compounds confirms the results reported in a previous work,[10] since the GC-MS extraction concentration technique used, previously validated by recovery trials with commercial standard solutions, is able to detect C_9 compounds in muskmelon. This phenomenon should be rather ascribed to the intrinsic features of the assayed material. Two causes could be put forward to explain this behaviour. The first might be linked to growing conditions (soil, fertilizer, climate, etc); this has little evidence because the raw material came from a typical area of muskmelon production. The second is connected to the selection of varieties. In fact, a recent survey on old Italian muskmelon varieties such as 'Viadanese' showed a very high content of odorous substances in comparison to new commercial varieties.[19] These changes should be studied as to how they are detected and appreciated by consumers.

Effect of chilled storage on aroma composition

Chilled storage had some influence on the general set of data. Ethylene content of the Pamir fruits at T_7

Table 3. Volatile composition by GC-HS technique of the two melon cultivars at three different ripening stages after harvest (T_0) and after 7 days of cold storage (T_7)

	Calypso T_0			Calypso T_7			Pamir T_0			Pamir T_7		
Compounds, $\mu g\,g^{-1}$ fw	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe
Acetaldehyde	312.62	485.72	6244.14	336.17	746.42	798.69	277.11	323.91	405.49	183.63	553.62	885.96
Methylformate	0.30	0.35	0.41	1.45	0.66	0.58	1.74	0.41	0.33	2.38	0.35	0.79
Ethylformate	1.95	1.83	2.01	0.87	2.92	2.57	0.45	3.08	3.96	0.26	1.18	3.27
Methylacetate	0.00	5.36	29.65	0.00	15.01	25.20	0.00	11.55	26.75	0.00	47.56	36.16
Ethylacetate	0.08a	87.74c	78.86bc	0.02a	47.73b	87.85c	0.12a	19.16b	71.61c	0.30a	179.88d	228.31d
Methanol	3173.91b	3134.16b	3502.72c	3261.91b	2607.13b	3607.74c	968.84a	3040.81b	3613.73c	988.38a	3319.6b	3933.63c
Isopropanol	6.77b	7.88b	10.65c	0.00a	31.43d	9.35c	48.86d	9.26b	9.37b	3.41b	10.70c	10.52c
Ethanol	610.05b	3140.55c	5177.27c	277.42a	4924.53c	41 525.54d	140.84a	1909.69b	3243.35c	229.11a	6811.43c	7696.72c
Ethyl propanoate	0.00	0.19	0.34	0.00	0.00	0.25	0.00	0.07	0.12	0.00	0.37	0.56
n-Propylacetate	0.00	0.89	1.58	0.00	0.27	1.45	0.00	0.23	0.17	0.00	1.60	1.83
Methylbutanoate	0.00	0.08	0.08	0.00	0.06	0.06	0.00	0.06	0.10	0.00	0.06	0.04
Isobutylacetate	0.00	1.21	1.35	0.27	0.33	1.25	0.00	1.41	1.71	0.00	1.52	1.50
Methyl 2-methyl-butanoate	0.00	1.14	2.16	0.00	0.48	2.09	0.00	0.43	0.77	0.00	1.93	2.33
Ethylbutanoate	0.00	0.15	0.00	0.00	0.20	0.32	0.00	0.13	0.13	0.00	0.21	0.36
Ethyl-2-methyl-butanoate	0.00	0.91	1.30	0.00	0.16	0.86	0.00	0.20	0.37	0.00	1.42	1.19
2-Methyl-1-butyl formate	0.00a	7.65b	8.65b	0.00a	6.53b	14.10c	0.00a	5.50b	5.15b	0.00a	16.61c	14.38c
n-Butyl acetate	0.00	0.22	0.17	0.06	0.08	0.10	0.10	0.11	0.07	0.15	0.18	0.14
2-Methyl-1-butyl acetate	2.62a	13.54c	15.71c	0.92a	6.34b	12.23c	0.00a	7.30b	10.28c	0.00a	7.52b	11.02c
2-Methyl-1-propanol	0.00a	4.83b	10.06c	0.00a	3.44b	7.80c	0.00a	2.72b	6.64bc	0.00a	14.83d	16.61d
***n*-Butanol**	0.00a	9.61b	12.07b	0.00a	4.30b	11.19b	0.00a	9.67b	12.89b	0.00a	10.14b	13.04b
2-Methyl-1-butanol	5.10b	17.90c	17.07c	2.30b	7.82bc	14.43c	0.00a	13.43c	16.25c	0.00a	14.68c	13.66c
Ethyl hexanoate	0.00	0.07	0.12	0.00	0.19	0.21	0.00	0.00	0.04	0.00	0.16	0.15
n-Hexyl acetate	0.00	0.76	1.78	0.00	0.00	0.88	0.00	0.42	1.12	0.00	0.76	0.80
***n*-Hexanol**	0.00a	12.63c	13.78c	0.00a	4.12b	13.07c	0.00a	9.39bc	13.61c	0.00a	9.50c	8.60bc
Total aromas	4113.4b	6935.36b	15 131.91c	3881.39ab	8410.16b	46 137.82d	1438.907a	5368.95a	7444.01b	1407.61a	11 005.82c	12 881.58c

Mean values of three replicates for each sample.
Compounds in bold are those considered in the correlation analyses.
Different letters in each row mean statistically significant difference ($p < 0.05$).

Table 4. Volatile composition by GC-MS extraction–concentration technique of the two melon cultivars at three different ripening stages after harvest (T_0) and after 7 days of cold storage (T_7)

	Calypso T_0			Calypso T_7			Pamir T_0			Pamir T_7		
Compounds, $\mu g\,g^{-1}$ fw	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe	Unripe	Ripe	Overripe
2-Butanone-3-hydroxy or acetoin	1.15a	7.99b	16.62c	0.55a	24.68c	18.06c	0.88a	7.73b	5.05b	3.09ab	25.97c	14.65bc
Ethylpropanoate	0.00	3.44	5.55	0.00	2.90	1.85	0.00	0.87	1.38	0.00	2.36	1.44
Propylacetate	0.00	3.18	2.78	0.58	4.92	2.08	0.00	2.96	3.49	0.00	4.53	3.26
Methylbutanoate	0.00	1.05	1.05	0.00	0.84	0.38	0.00	0.87	1.01	0.00	0.67	0.40
3-(*E*)-penten-2-one	0.00	0.88	0.00	0.56	0.00	0.55	0.00	0.97	0.54	0.25	1.13	0.83
2-Methyl-1-butanol	2.74a	42.35d	26.38c	1.48a	21.75c	13.96b	1.04a	26.28c	19.14c	0.45a	9.37b	12.91b
Ethyl-2-methylpropanoate	0.00	1.35	3.90	0.00	0.76	0.73	0.00	0.45	0.56	0.00	0.66	0.63
1-Pentanol	0.00	0.00	0.00	0.00	0.00	0.00	1.82	2.14	0.00	0.00	1.14	0.00
Isobutylacetate	1.26	5.62	6.40	0.69	3.96	5.39	0.00	5.25	6.59	0.00	3.30	7.27
Methyl-2-methylbutanoate	0.74	6.24	4.12	0.53	2.06	0.00	0.00	2.71	2.69	0.26	2.87	1.97
Ethyl butanoate	0.00a	12.28c	19.86c	0.00a	9.77b	9.47b	0.37a	4.01b	6.88b	0.18a	8.52b	5.39b
***n*-Butyl acetate**	0.00a	8.71c	7.00c	0.00a	0.00a	4.88b	0.00a	7.93c	10.25c	0.00a	0.00a	4.71b
Ethanol-2-(methylthio)	0.00	0.00	0.00	0.00	0.53	0.54	0.00	1.59	0.00	0.00	0.00	0.77
Ethyl-2-methylbutanoate	0.00	8.76	15.26	0.00	5.36	3.44	0.00	1.69	2.29	0.31	4.57	2.53
3-(*Z*)-hexen-1-ol	0.00	1.41	2.38	0.00	0.00	1.59	0.00	0.00	0.00	0.00	0.00	0.00
***n*-Hexanol**	0.50a	12.17c	12.80c	0.00a	6.08b	5.78b	0.00a	14.06c	8.51bc	0.00a	2.48b	3.53b
2-Methyl-1-butyl acetate	2.37a	13.48c	7.57b	1.32a	7.01b	4.12b	0.29a	10.49c	11.42c	0.34a	6.30b	6.59b
Propanal-3-(methylthio)	0.00	0.34	0.00	0.00	0.37	0.37	0.00	0.33	0.00	0.18	0.00	0.22
Pentyl acetate	0.00	0.36	0.00	0.00	0.00	0.27	0.00	0.32	0.41	0.00	0.36	0.19
Ethyl-2-(methylthio) acetate	0.00	0.45	2.72	0.00	2.09	1.08	0.00	0.33	0.00	0.00	0.00	2.90
Ethyl hexanoate	0.50	0.55	2.23	0.00	1.65	1.50	0.00	0.50	0.65	0.00	1.11	0.77
***n*-Hexyl acetate**	0.53b	12.81d	9.64c	0.66b	6.65c	5.45c	0.00a	12.41d	10.80d	2.67bc	4.78c	5.29c
Benzyl alcohol	0.00	7.90	3.23	0.00	2.86	6.38	0.00	13.33	3.58	6.33	4.39	4.13
Ethyl-3-(methylthio)propanoate	0.00	0.00	0.00	0.00	0.81	0.67	0.00	0.00	0.00	0.00	0.00	0.00
Propyl-3-(methylthio)acetate	0.00	0.00	0.00	0.00	0.68	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,6-(*E*-*Z*)-nonadienal	0.00	0.00	0.00	0.00	0.00	0.00	1.20	0.00	0.00	0.00	0.00	0.00
2-(*E*)-nonenal	0.00	0.00	0.00	0.00	0.00	0.00	2.09	0.00	0.00	0.00	0.00	0.00
Total aromas	9.78a	151.33c	149.50c	6.36a	105.73b	88.51b	7.69a	117.21c	95.23b	14.05a	84.5b	80.39b

Mean values of three replicates for each sample.
Compounds in bold are those considered in the correlation analyses.
Different letters in each row mean statistically significant difference ($p < 0.05$).

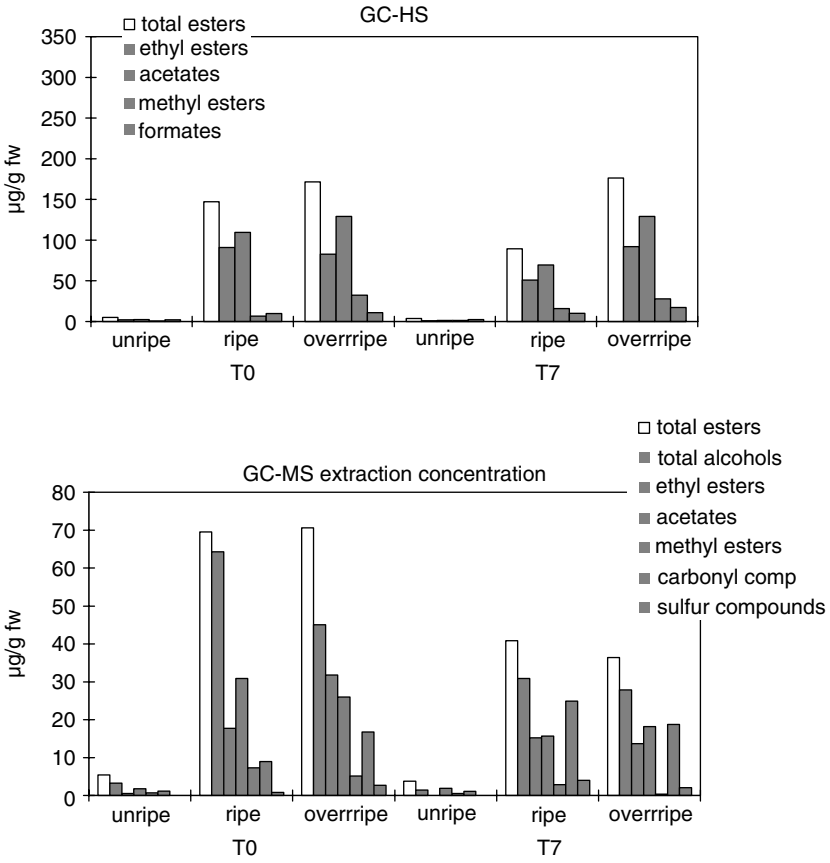

Figure 1. Amounts of the main volatiles classes of compounds in Calypso variety extracted with two different techniques at T_0 and at T_7.

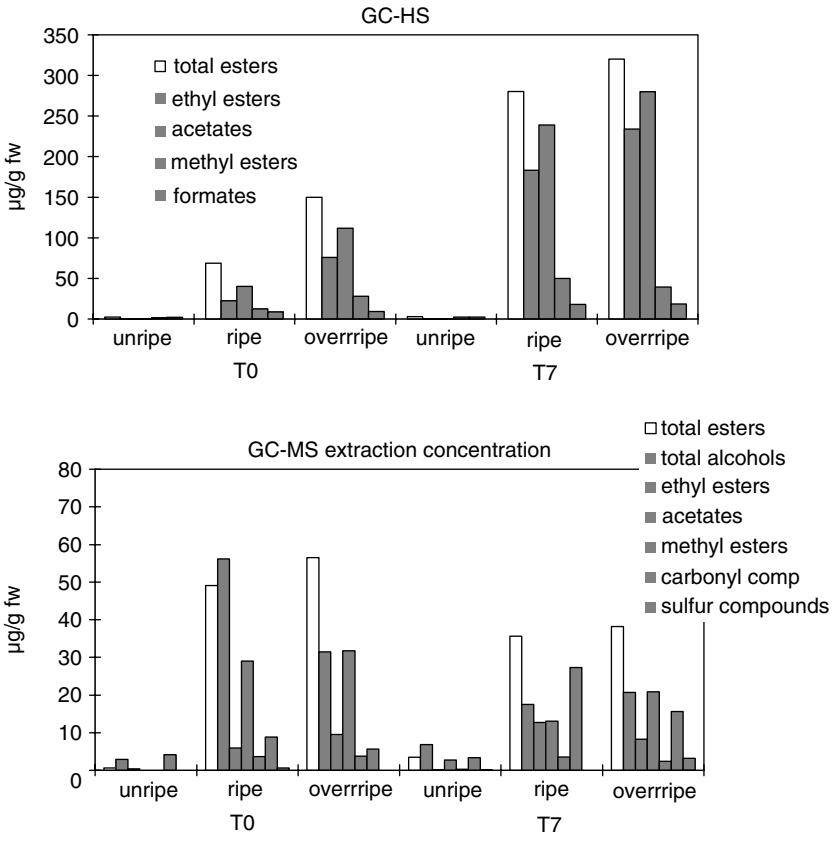

Figure 2. Amounts of the main volatiles classes of compounds in Pamir variety extracted with two different techniques at T_0 and at T_7.

showed a peak value at the ripe stage but the value was much lower than that at T_0. This confirms once more that the ripe fruits were picked at the right time. The cv Calypso at T_7 was an exception, because the values of ethylene production showed a continuous increase from unripe to overripe fruits, even if the values were much lower than at T_0. This means that Calypso has a specific pattern of ethylene production.

The differences in colour parameters noted at T_0 in overripe fruits with respect to ripe ones presented some changes at T_7. The overripe melons of the Calypso variety showed significant differences only for brightness (L^*), which increased, while hue and saturation remained quite stable. The Pamir variety behaved differently: brightness decreased even at the ripe stage while hue and saturation increased at ripe and overripe stage (Table 1).

The analysis of single sugars by HPLC showed that the varieties behaved differently for the sucrose content. The unripe samples of Calypso fruits had an increase after 7 days of storage, while the fruits of Pamir variety had a decrease. This was considered as a sign of the different metabolic behaviour of the two varieties. Pamir once again seemed to be less susceptible to overripening, as was also confirmed by the ethanol data.

Moreover, there was a large increase of total esters, ethyl esters, acetates and formates in the HS aroma profile of Pamir fruits at T_7 with respect to T_0 (Fig 2). Calypso fruits did not show any increase (Fig 1). On the other hand, after cold storage there was a general decrease in esters and alcohols in the aroma profiles from the extraction–concentration GC-MS samples. The carbonyl compounds were significantly higher than those found at T_0 (Figs 1 and 2).

The evolution of the individual aroma compounds during the chilled storage demonstrated that the main ester component detected by GC-HS, ie 2-methyl-1-butyl acetate decreased in Calypso fruits and remained quite stable in Pamir fruits (Table 3). The 2-methyl-1-butyl formate increased in all the samples of Pamir fruits while in Calypso samples the increase is noted only in the overripe fruits.

The main aroma compounds of extraction–concentration GC-MS, ie ethylbutanoate, ethyl-2-methylbutanoate and hexyl acetate generally decreased after storage, with the exception of ethyl butanoate and ethyl-2-methylbutanoate in ripe fruits of cv Pamir (Table 4). These findings reinforce the hypothesis that Pamir has a better retention of its aroma profile after storage. As regards acetoin (Table 4), there was an increase after storage in ripe samples of both varieties.

Correlation between sensory descriptors, biochemical parameters and ripening stage

Very high values arose from the correlation analysis performed between the sensory descriptors and between the classes of aroma compounds detected with GC-HS. The sensory descriptors presented striking correlations, but the more interesting ones regarded flavour, sweetness and juiciness, which were very strictly connected with acceptance [Table 5(A)]. This evidence confirms the issues reported previously.[10] Regarding single sugars, high values were found for sucrose, especially during ripening (0.67) [table 5(B)], while glucose and fructose were negatively correlated with sweetness and ripening stage, meaning an evident decrease during ripening.

Strong correlations also existed between the instrumental texture determined by dynamometer and sensory firmness (0.77) [Table 5(C)] as well as between sensory sweetness and the solid soluble content (0.64) [Table 5(B)].

A low and non-significant correlation was found between ethylene content of the fruit and instrumental firmness. This means that as ethylene production increased firmness decreased, continuing to do so even when ethylene production decreased.

The correlation between the aroma profile from HS total volatiles and sensory flavour analysis (Table 6) gave low value (0.18), but the good correlation was much more interesting between sensory flavour and total esters, ethyl esters, acetates, methyl esters and formates (Table 6). The high correlation value found for formates (0.70) confirms the results reported in a previous work.[10]

A relevant consideration concerns the fact that no correlation was found between sensory flavour and total alcohols (0.16). This could be explained by the fact that alcohols were mainly represented by ethanol, which could have given a fermented note not well appreciated by the panellists. However, high correlation existed between sensory flavour and other single alcohols such as 2 methyl-1-propanol, *n*-butanol and *n*-hexanol.

Table 5. Correlation coefficients between the descriptor sensory acceptance and ripening stage with some sensory descriptors (A), between sweetness and ripening stage with sugars (B), and between firmness, ripening stage with some related biochemical parameters (C)

(A)		*Acceptance*	*Ripening stage*
	Flavour	0.91*	0.75*
	Sweetness	0.89*	0.68**
	Juiciness	0.90*	0.74*
	Firmness	−0.74*	−0.73*
	Acceptance vs ripening stage 0.76		
(B)		*Sweetness*	*Ripening stage*
	Soluble solids	0.64**	0.76*
	Sucrose	0.58	0.67*
	Glucose	−0.55	−0.89*
	Fructose	−0.51	−0.81*
	Total HPLC sugars	0.50	0.48
(C)		*Firmness*	*Ripening* stage
	Dynamometer	0.77*	−0.83*
	Ethylene	−0.29	0.30
	Methanol	−0.36	0.67**
	Methyl esters	−0.56	0.76*

* Significant at $p < 0.01$; ** significant at $p < 0.05$.

Table 6. Correlation coefficients between the descriptor sensory flavour and ripening stage with the classes of volatile compounds evaluated by GC-HS, the main single alcohols, and the main single esters

Classes of compounds	Flavour	Ripening stage
Total HS volatiles	0.18	0.51
Total esters	0.66**	0.74*
Total alcohols	0.16	0.49
Ethyl esters	0.61**	0.65**
Acetates	0.64**	0.71*
Methyl esters	0.64**	0.76*
Formates	0.70**	0.79**
Alcohols		
Methanol	0.45	0.67**
Isopropanol	−0.13	−0.15
Ethanol	0.13	0.42
2-Methyl-1-propanol	0.66**	0.75*
n-Butanol	0.78*	0.93*
2-Methyl-1-butanol	0.72*	0.85*
n-Hexanol	0.73*	0.89*
Esters		
Ethyl acetate	0.60**	0.64**
2-Methyl-1-butylformate	0.64**	0.73*
2-Methyl-1-butylacetate	0.68**	0.89*

* Significant at $p < 0.01$; ** significant at $p < 0.05$.

Table 7. Correlation coefficients between the descriptor sensory flavour and ripening stage with the classes of volatile compounds evaluated by GC-MS concentration–extraction with the main single alcohols, and the main single esters

Classes of compounds	Flavour	Ripening stage
Total volatiles	0.67**	0.74*
Total esters	0.69**	0.78*
Total alcohols	0.55	0.58
Ethyl esters	0.51	0.70*
Acetates	0.72*	0.80*
Methyl esters	0.54	0.47
Carbonyl compounds	0.51	0.55
C9 compounds	0.13	0.20
Sulphur compounds	0.40	0.57
Alcohols		
Acetoin	0.51	0.56
2-Methyl-1-butanol	0.44	0.42
n-Hexanol	0.52	0.59**
Esters		
Ethyl butanoate	0.46	0.60**
n-Butyl acetate	0.54	0.59
2-Methyl-1-butylacetate	0.38	0.36
n-Hexylacetate	0.56	0.55

* Significant at $p < 0.01$; ** significant at $p < 0.05$.

The correlations between sensory flavour and single esters were also significant, above all, those with 2-methyl-1-butanolacetate and with 2-methyl-1-butanolformate, confirming the previous results for these classes of compounds.

The correlation between the sensory flavour and the classes of compounds found by means of the GC-MS extraction-concentration technique (Table 7) confirmed the high correlation with total esters, especially acetates, while total alcohols gave a lower value (0.55). A high value was found for sensory flavour and total volatiles (0.67), in contrast with the HS data. This could be due to the different techniques used for aroma recovery; for example the extraction–concentration technique did not detect the highly volatile compounds (ie ethanol), while it was more suitable for compounds with higher evaporating temperatures.

As regards the individual compounds, lower values were found than in HS data; the highest correlation was found for *n*-hexyl acetate, but it was not significant (0.56). There was also an interesting correlation between the sensory descriptor acceptance and ripening stage (0.76, Table 5), mainly caused by the relevant changes of aroma compounds, sugars and firmness, which occurred as melon fruits passed from unripe to ripe stage.

The correlation values between volatile compounds and ripening stage were generally higher than the correlation between volatile compounds and sensory flavour (Tables 6 and 7). As the correlations between sensory descriptors and ripening stage were lower than the correlations between sensory descriptors and acceptance [Table 5(A)], it could be argued that the increase in the volatile compounds with ripening is not always well appreciated by the panellists. This was probably due to the increase of off-flavours such as ethanol.

The highest value for aroma compounds revealed by HS was for *n*-butanol (0.93) (Table 6), while in the extraction–concentration technique the highest value was for the total acetates (0.80) (Table 7).

A further consideration regards the correlation between sensory flavour and acetoin (2-butanone-3-hydroxy), which reached a low value of 0.51, while the correlation with ripening stage was 0.56 (Table 7).

An important point to be considered is that in these cultivars the C_9 compounds, which are considered as characteristic of the melon aroma, were found in very low amounts by our methods. A possible explanation could be that the genetic improvement in the melon varieties had a negative effect on some aroma compounds, which were considered as typical components of aroma of old melon varieties.[19]

CONCLUSIONS

Sensory characteristics play a remarkable role in the acceptance of melon fruits. The sensory descriptor flavour had the highest correlation value with the acceptance. The ripening stage had a fundamental role for the aroma content of fruits. Very noticeable changes can be induced in the volatiles content if the melon fruits are harvested 2 days earlier or later. However, overripe fruits are not better appreciated than ripe fruits, probably because of the presence of ethanol.

The most important effect of the volatile compounds on the intensity of sensory descriptor flavour should be

ascribed to the esters, especially formates and acetates. Alcohols with four to six carbon atoms also greatly influenced the aroma acceptance, while total alcohols were poorly correlated with aroma.

The cold storage induced some changes in the aroma profile, in particular for total esters; GC-HS data showed a tendency to increase, while GC-MS extraction concentration data showed a marked decrease.

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