Research Article

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Aroma volatiles recovered in the water phase of cashew apple (*Anacardium occidentale* L.) juice during concentration

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Abstract

BACKGROUND: There is a considerable loss of volatile compounds during the thermal concentration of cashew apple juice, damaging product quality, and as yet there is little research on the subject. Thus the purpose of this research was to identify the aroma volatiles evaporated off from cashew apple juice and recovered in the water phase during concentration of this beverage in an industrial plant. Water phase volatiles were extracted using dichloromethane, concentrated under a nitrogen flow, separated by gas chromatography (GC) and identified by GC-mass spectrometry. In order to determine the contribution of each volatile to the cashew aroma, five trained judges evaluated the GC effluents using the Osme GC-olfactometry technique.

RESULTS: 71 volatiles were identified; of these, 47 were odour active. Alcohols were preferentially recovered in the cashew water phase, notably heptanol, *trans*-3-hexen-1-ol and 3-methyl-1-butanol, representing 42% of the total chromatogram area and imparting green grass and fruity aroma notes to the water phase. Esters represented 21% of the total chromatogram area, especially ethyl 2-hydroxyhexanoate, ethyl *trans*-2-butenoate and ethyl 2-methylbutanoate, and were responsible for the fruity/cashew-like aroma of the water phase. On the other hand, 3-methylbutanoic and 2-methylbutanoic acids were the volatiles that presented the greatest odour impact in the GC effluents of the water phase.

CONCLUSION: Overall, the results of the present study strongly indicated that further concentration of the esters recovered in the water phase, either by partial distillation or by alternative technologies such as pervaporation, could generate a higher-quality natural cashew apple essence.
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Keywords: volatile compound; cashew apple; *Anacardium occidentale*; gas chromatography-mass spectrometry; aroma; water phase

INTRODUCTION

Thermal processing usually reduces the sensory quality of fruit juices, attributed mainly to: (i) the loss, either by evaporation or degradation, of the volatile compounds responsible for the typical aroma and flavour of the fresh fruit; and/or (ii) the formation of additional odour volatiles that have a negative impact on the aroma and flavour of the juice.[1-3] In the juice of cashew apple, a pseudo-fruit native to Brazil, which possesses an exotic and pleasant aroma and flavour, the loss of volatile compounds during thermal processing seems to occur to a great extent, as suggested by the studies cited below.

The studies of Macleod and Troconis,[4] Maciel *et al*.,[5] Maia *et al*.,[6] Bicalho *et al*.,[7] Garruti *et al*.,[8] Valim *et al*.[9] and Cardeal *et al*.[10] on cashew apple juice suggest the existence of a considerable difference between the fresh and processed products with respect to their volatile profiles. For instance, while Valim *et al*.[9] only found 12 esters in a cashew apple juice reconstituted from a commercial concentrated nectar, a significantly higher number of esters were identified by Maciel *et al*.[5] (21 esters), by Bicalho *et al*.[7] (27 esters) and by Garruti *et al*.[8] (23 esters) in the fresh fruit or its fresh juice. Of the esters identified by Garruti *et al*.[8] as important volatiles in the fresh cashew apple aroma and

flavour, such as ethyl acetate, methyl butanoate, methyl 3-methylbutanoate, ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate, methyl 3-methylpentanoate and ethyl *trans*-2-butenoate, only ethyl butanoate, ethyl 2-methylbutanoate and ethyl 3-methylbutanoate were found by Valim *et al*.[9] in their reconstituted cashew apple juice. These data strongly suggest that thermal processing leads to a drastic loss of cashew apple aroma volatiles.

To minimize the loss of sensory quality in processed juices, notably in concentrated juices, the food industry recovers the volatile compounds evaporated off from the juice during concentration by partial condensation and distillation, amongst

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other techniques.[11] The recovered material is a water-volatile mixture weighing from 15%[12] to 30%[13,14] of the original juice. This mixture is subsequently concentrated to strengths ranging from 1:100 to 1:150, usually by distillation, generating an aroma concentrate known as the water phase, which is added back to the processed juice to recover its natural aroma and flavour.[14,15]

While the recovery of aroma volatiles evaporated off during the concentration of orange juice is technologically well established,[16–18] and orange water phases of good quality are currently available, the same cannot be said for several tropical fruit juices and notably for cashew apple juice. In fact, there is a general distrust amongst the Brazilian juice plants with respect to the ability of their cashew apple water phases to recover the natural aroma and flavour in their processed juice.

Optimizing the recovery and concentration of the volatiles lost during juice concentration is not trivial. It requires prior knowledge of which volatiles evaporate from the juice during processing and the importance of each individual aroma to the fresh fruit aroma and flavour. For this reason, research has been carried out to identify the volatile compounds evaporated off and recovered during beverage concentration for several fruits, such as mangoes, pineapples, guavas,[19] apples,[15,20] grapes, apricots, peaches, strawberries and mulberries.[15] This knowledge allows researchers and engineers to explore not only the optimization of traditional recovery methods, but also the combined use of modern alternative technologies such as pervaporation,[21–24] to recover volatiles lost during juice concentration. Unfortunately, with respect to cashew apple juice, with the exception of the study by Ramteke *et al.*,[19] there is little published data on the subject.

Hence the purpose of the present research was to identify the volatile compounds evaporated off from the juice and recovered in the water phase during the concentration of cashew apple juice at an industrial level, assessing the aroma significance of each volatile. The study explored the subject under the conditions actually practised by the Brazilian juice plants, generating important information for this economic segment, which currently exports approximately US $1.3 billion per year and employs 27% of the national agricultural workforce.[25–27] In this context, the cashew apple culture is gaining competitiveness, having grown from 1.1 million tons per year in 2001[28] to 1.7 million tons per year in 2009,[29] and employing about 300 000 direct and indirect workers.[30] Approximately 10% of the fruit production is processed by the juice industry.[30]

MATERIAL AND METHODS
Raw material
Cashew apples cultivated in the State of Ceará, Brazil, were harvested manually, the nuts removed and the fruits carefully placed in 10 kg perforated plastic boxes and transported to the processing plant. On arrival at the plant, the fruits were weighed and green or damaged fruits discarded. The remaining apples were sanitized by immersion in a 100 ppm free chlorine solution for 20 min and then rinsed with running water.

Juice extraction and concentration
The cashew apples were crushed in an expeller press in an atmosphere of steam, to avoid enzymatic activity in the juice. The resulting material was passed through a finisher (0.8 mm) and then through a line filter to reduce the pulp content, and the juice was transferred to a tank where it was homogenized (101 kPa)

and de-aerated (80 kPa). Finally, the beverage was concentrated in a four-stage concentrator (first and second stages using a plate evaporator (APV, London, UK), the third stage using a falling film shell and tube evaporator and the fourth stage using a scraped surface evaporator (Rossi & Catelli, Parma, Italy). The concentration temperature was 59 °C under vacuum (85 kPa) to a final value of 45° Brix.

Recovery of volatiles in the water phase
The volatile compounds lost by evaporation during concentration of the juice in the first stage were recovered using an aroma recovery equipment (Rossi & Catelli) and collected in 60 L plastic containers. The water phase obtained was frozen and stored at −15 °C until analysed.

Sensory evaluation of the water phase
The aroma of the cashew apple water phase was evaluated by a sensory panel of 10 trained judges, all of whom were either students or employees at the Food Engineering Faculty of the University of Campinas (FEA/UNICAMP, São Paulo, Brazil).

For training purposes, each individual received both whole and diluted fresh cashew apple juice at juice:water strengths of 1:1, 1:2, 1:4, 1:10, 1:20 and 1:40. During training, the samples (40 mL) were served in opaque wine glasses covered with watch glasses. The subjects were asked to sniff the samples, evaluate the intensity of the fresh cashew apple aroma and grade them on a 9 cm unstructured scale, anchored at the left and right extremes by the terms 'weak' and 'strong', respectively. The subjects were informed that the 1:40 and 1:1 dilutions exemplified fresh cashew aromas of weak and strong intensities, respectively. The 1:10 and 1:4 dilutions exemplified fresh cashew aromas of moderate intensity.

At the end of the training period, a test was performed in which each participant rated the aroma of fresh cashew apple in three samples (1:4, 1:10 and 1:20 dilutions of whole cashew juice, respectively) using the above-mentioned scale. The test was repeated three times, with the participants in individual booths with red lighting to mask any possible visual difference amongst the samples.

An analysis of variance (ANOVA) was then carried out for each subject, and the levels of significance (P) for F_{sample} and $F_{repetition}$ were computed. Individuals showing high sample discrimination power ($P\ F_{sample} \leq 0.05$), ability to reproduce their judgments ($P\ F_{repetition} \geq 0.05$) and good agreement with the other panellists were chosen to be members of the trained sensory panel.[31,32]

Finally, for each judge, a 7 µL aliquot of the water phase was transferred to a paper strip (IFF Essences and Fragrances, Taubaté, Brazil), and immediately after solvent evaporation, was submitted to the judge, who rated its intensity of fresh cashew aroma and described additional aromatic notes. Transference of the sample to the paper strip was necessary in order to avoid solvent inhalation by the panellists. The researcher carried out the sample transference and submission to each judge.

Isolation of the volatiles recovered in the water phase
The volatile compounds present in the water phase were extracted with dichloromethane and concentrated under a nitrogen flow.[33]

To verify if the method was efficient in isolating the odour volatiles from the water phase, 7 µL of the isolate was transferred to a paper strip (IFF Essences and Fragrances) and submitted to the trained sensory panel. The judges rated the intensity of the

cashew aroma on a 9 cm unstructured scale, and described any additional aromatic notes perceived in the isolate. A statistical test (t-test) was performed to compare the intensity of the fresh fruit aroma present in the water phase to that perceived in the isolate. The frequency with which the judges cited each additional aromatic note was also computed.

Gas chromatographic analysis

The isolate containing the volatile compounds present in the water phase was analyzed in replicate using a Varian 3600 (Palo Alto, CA, USA) high-resolution gas chromatograph equipped with a flame ionization detector (FID). A DB-Wax (JW Scientific, Folsom, CA, USA) fused-silica capillary column (30 m × 0.25 mm, 0.25 µm) was maintained at 35 °C for 9 min, raised to 80 °C at 5 °C min^{-1}, then to 100 °C at 1 °C min^{-1}, and finally to 210 °C at 16 °C min^{-1}, and maintained at 210 °C (T_{final}) for 20 min, giving a total of approximately 65 min of analysis. The splitless mode injector was maintained at 230 °C and the FID at 260 °C. Hydrogen was the carrier gas at a linear velocity of 51.5 cm s^{-1}. The sample volume injected was 2 µL. Additionally, a C7–C28 series of straight-chain alkanes (Polyscience 211 C kit, Chicago, IL, USA) were dissolved in dichloromethane, and the solution injected in the gas chromatograph, operating under the same conditions. Thus the retention index of each volatile compound detected by the FID of the gas chromatograph was calculated as recommended by Van Den Dool and Kratz.[34] The indices helped the identification of the odour volatiles perceived by the sensory panel in the GC effluents.

Gas chromatography–mass spectrometry (GC-MS)

The volatiles present in the isolate were identified in a Shimadzu 17-A gas chromatograph coupled to a Shimadzu QP-5000 mass spectrometer (Kyoto, Japan), operating under an ionization voltage of 70 eV, scan mode and m/z range from 35 to 350. The column and oven conditions were the same as those used for the GC-FID analysis. Helium was the carrier gas, at a linear velocity of 46 cm s^{-1}. The injection volume was 3 µL.

Identification of volatiles

To help with identification of the volatile compounds, linear retention indices (LRI) were calculated for the GC-MS data and compared with indices reported in the literature.[8,9,35,36] Thus a C7–C28 series of straight-chain alkanes (Polyscience 211 C kit) were dissolved in dichloromethane, and the solution injected into the gas chromatograph–mass spectrometer, operating under the same conditions described above. The retention index of each compound was calculated as recommended by Van Den Dool and Kratz.[34]

Individual compounds were identified by: (i) comparing the experimentally obtained mass spectra of the compound with those provided by the Wiley and Nist libraries; (ii) comparing the volatile retention index obtained using the DB-Wax column with the retention indices published in the literature for columns with the same polarity;[8,9,35,36] and (iii) comparing the volatile mass spectra with the mass spectra of pure compounds analysed in the same gas chromatograph–mass spectrometer using the same methodological conditions.

The compounds were considered positively identified if their mass spectra and retention indices were comparable to those of the pure standards analysed under the same conditions. The compounds were considered identified when their mass

Table 1. Mean intensity[a] of fresh cashew apple aroma in water phase and related isolate (n = 10 judges)

Sample	Intensity of cashew apple aroma[a] (± standard deviation)
Water phase	5.67 (±1.94)
Water phase isolate	6.46 (±2.14)
P_{t-test}[b]	0.09

[a] 0 = weak (juice dilution, 1 : 40); 9 = strong (juice dilution, 1 : 1).
[b] Level of significance in the t-test between mean intensity observed in water phase and respective isolate.

spectra matched those available in the computerized library and their retention indices were similar to those reported in the literature.[8,9,35,36] Finally, compounds were considered tentatively identified when their identification was based solely on their mass spectrometric data.

Aroma volatiles in the water phase

The odour significance of the volatiles present in the water phase was assessed using the Osme GC–olfactometry technique (GC-O).[8] For this analysis, the Varian 3600 gas chromatograph described above was modified, and the DB-Wax capillary column was moved from the FID detector to another base detector heated at 250 °C. A sniffer, consisting of a 60 cm × 1 cm silanized glass tube (98% trimethylchlorosilane, Acros Organics, Geel, Belgium) was placed on top of the above-mentioned detector base to direct the GC effluents to the judge's nose. GC effluents leaving the DB-Wax column were mixed with heated (28 °C), humidified charcoal-filtered air (4 L min^{-1}) and directed to the judge's nose. The chromatographic conditions were the same as previously described. Five judges from the trained panel participated in the GC-O analysis (three women and two men, ranging from 24 to 38 years old). Using a computer mouse, each judge rated the intensity of each odour perceived in the GC effluent using a 10-point scale located on the computer monitor (0 = none; 10 = extreme). In addition, the judges described the odour quality of each odorant to the researcher. Time and intensity values were registered and stored using SCDTI software developed at UNICAMP, Campinas, Brazil. The cashew apple water phase was analysed in triplicate by each judge. The judges evaluated the 65 min chromatographic run in two independent sessions of 32.5 min each.

For each judge, after making his/her GC-O analysis, the SCDTI software generated an individual aromagram named an Osmegram. The Osmegram represented the judge's perception of each odorant present in the GC effluent, as a peak similar to those drawn in the chromatogram. For each odour peak, the SCDTI also reported the corresponding maximum intensity, odour duration and area.[8]

A consensus Osmegram was constructed for the water phase isolate, averaging all the peaks detected twice by at least two judges.

RESULTS AND DISCUSSION
Water phase sensory attributes

As shown in Table 1, the aroma note described as 'fresh cashew apple' was present in the water phase at a moderate intensity, demonstrating that volatiles important to this sensory note were

Table 2. Aroma notes (% of citations) in addition to that of fresh cashew apple perceived by the sensory panel in the water phase and in its related isolate ($n = 10$ judges)

Descriptor	Water phase (%)	Isolate (%)
Fruity	25.0	35.6
Sweet/candy	31.2	16.9
Floral	12.5	11.8
Strawberry	12.5	3.4
Fermented overripe fruit	12.5	6.8
Woody	6.2	6.8

in fact lost during juice concentration, and recovered in the water phase.

Table 1 also indicates that there was no significant difference ($P = 0.09$) between the water phase and its isolate with respect to their intensity of fresh cashew aroma. This confirms that the volatile compounds responsible for this aroma note in the water phase were successfully isolated.

Finally, Table 2 shows that both the water phase and the isolate presented additional aromatic notes, described by the sensory panel as 'sweet' (or 'candy'), 'fruity', 'floral' 'overripe fruit' and 'wood', most of these descriptors being consistent with odour compounds previously identified in fresh cashew apple juice by the current research group.[8]

Volatiles recovered in the water phase

The water phase contained 76 volatile compounds, of which 71 were identified, as shown in Table 3. The majority of the volatiles identified in the water phase were esters (27 compounds), followed by alcohols (21), acids (11), aldehydes (4), ketones (4), lactones (3) and one hydrocarbon (1).

Alcohols were the volatiles present in the highest proportion in the water phase, representing 42% of the total area of the chromatogram (Table 3). Esters were the class of compounds present in the second highest proportion in the water phase, representing 21% of the total area of the chromatogram, followed by acids (13%), ketones and lactones (13%).

Of the alcohols, 3-methyl-1-butanol was the major compound, representing 24% of the total area of the chromatogram (Table 3), followed by cis-3-hexen-1-ol (4.5%) and hexanol (4.1%).

Ethyl 2-hydroxy-4-methylpentanoate was the most abundant ester found in the water phase. It represented approximately 14% of the total area of the chromatogram and was followed by ethyl 3-methylbutanoate (3%) and a series of other esters, such as ethyl 2-methylbutanoate (1%), ethyl hexanoate and ethyl *trans*-2-methyl-2-butenoate (0.7%), occurring in minor proportions (Table 3).

Two ketones were present in high proportions in the water phase: 3-hydroxy-2-butanone, corresponding to approximately 7% of the total area of the chromatogram, and 2,3-butanedione (3.3%) (Table 3). One lactone, γ-dodecalactone, was present in noticeable amounts (2.1%). Of the acids, the mixture of 2-methyl-butanoic and 3-methylbutanoic acids represented 11.6% of the total area of the chromatogram, accounting for almost the whole amount of acids present in the water phase. Finally, Table 3 shows that the aldehydes were only minor volatiles in the water phase, *trans*-2-hexenal being the most abundant (1.5%).

The number of alcohols identified in the water phase (21) was higher than that reported by most researchers for cashew juice.

Table 3. Volatile compounds identified in the cashew apple water phase and respective area (%) of the chromatogram

LRI (DB-Wax)	Compound	% Area (FID)
	Ester	20.99
<1000	Ethyl propanoate[b]	0.12
<1000	Ethyl 2-methylpropanoate[b]	0.16
1010	Methyl 2-methylbutanoate[b]	tr
1014	Methyl 3-methylbutanoate[a]	0.15
1032	Ethyl butanoate[a]	0.17
1048	Ethyl 2-methylbutanoate[a]	0.97
1067	Ethyl 3-methylbutanoate[a]	3.31
1115	Methyl *trans*-2-butenoate[b]	0.03
1127	Isoamyl acetate[a]	0.05
1166	Ethyl *trans*-2-butenoate[a]	0.04
1182	Ethyl 3-methylpentanoate[b]	0.04
1203	Methyl 2-ethylacrylate[c]	tr
1237	Ethyl hexanoate[a]	}0.69
1239	Ethyl *trans*-2-methyl-2-butenoate[a]	
1298	Ethyl *trans*-3-hexenoate[b]	0.05
1338	Ethyl *trans*-2-hexenoate[b]	0.09
1407	Ethyl 3-hydroxy-3-methylbutanoate[c]	0.24
1429	Ethyl octanoate[b]	tr
1486	Methyl 2-hydroxy-3-methylpentanoate[b]	0.03
1522	Methyl 2-hydroxy-4-methylpentanoate[c]	0.34
1547	Ethyl 2-hydroxy-4-methylpentanoate[b]	13.97
1596	Ethyl 2-hydroxyhexanoate[b]	0.12
1662	Ethyl decanoate[b]	tr
1696	Ethyl 3-hydroxyhexanoate[b]	0.04
1800	2-Phenylethyl acetate[b]	0.08
1936	3-Phenylpropyl acetate[c]	tr
2134	Ethyl cinnamate[b]	0.30
	Alcohol	42.06
1038	2-Methyl-3-buten-2-ol[b]	0.29
1096	2-Methyl-1-propanol[a]	1.62
1119	3-Pentanol[b]	0.05
1159	1-Butanol[a]	0.36
1173	1-Penten-3-ol[b]	0.98
1178	3-Buten-1-ol[b]	0.72
1226	3-Methyl-1-butanol[a]	24.03
1262	1-Pentanol[a]	0.95
1314	*Trans*-2-Penten-1-ol[b]	0.10
1318	4-Methyl-1-pentanol[b]	0.29
1323	Cyclopentanol[c]	0.91
1330	3-Methyl-1-pentanol[b]	0.56
1359	Hexanol[b]	4.11
1366	*Trans*-3-Hexen-1-ol[b]	0.94
1388	cis-3-Hexen-1-ol[a]	4.52
1409	*Trans*-2-Hexen-1-ol[b]	0.36
1460	Heptanol[b]	0.14
1502	2-Ethyl-1-hexanol[b]	0.10
1566	1-Octanol[a]	0.39
1907	Phenylethyl alcohol[b]	0.45
2049	3-Phenyl propanol[b]	0.19
	Aldehyde	1.94
1074	Hexanal[a]	0.11
1141	2-Methyl-4-pentenal[c]	0.12
1209	*Trans*-2-Hexenal[b]	1.54
1451	Furaldehyde[b]	0.17
	Ketone/lactone	12.88
<1000	2,3-Butanedione[b]	3.30

Table 3. (Continued)

LRI (DB-Wax)	Compound	% Area (FID)
1055	2,3-Pentanedione[b]	0.07
1282	3-Hydroxy-2-butanone[a]	7.08
1628	Acetophenone[b]	0.38
1721	γ-Hexalactone[b]	tr
2025	γ-Nonalactone[b]	tr
2399	γ-Dodecalactone[b]	2.05
	Acids	12.62
1445	Acetic acid[b]	tr
1566	2-Methylpropanoic acid[b]	tr
1667	3-Methylbutanoic acid[b]	11.63
1667	2-Methylbutanoic acid[a]	
1846	Hexanoic acid[a]	0.34
1873	Benzylic acid[b]	0.03
2058	Octanoic acid[b]	0.27
2176	Nonanoic acid[b]	0.08
2271	Decanoic acid[b]	0.27
2484	Undecanoic acid[b]	tr
2560	Phenylacetic acid[b]	tr
	Hydrocarbon	0.11
1248	Benzocyclobutene[c]	0.11
	Unidentified compounds	5.09
1379	NI	1.05
1414	NI	tr
1513	NI	2.85
1951	NI	tr
2437	NI	1.19

NI, compound not identified; tr, detected in trace amounts (<0.01%).
[a] Compound positively identified (pure standard).
[b] Compound identified by MS and linear retention index.
[c] Compound tentatively identified.

Macleod and Troconis[4] identified two alcohols; Maciel et al.,[5] eight; Maia et al.,[6] five; Bicalho et al.,[7] four; Garruti et al.,[8] eight; Valim et al.,[9] two; Cardeal et al.,[10] one; and Carasek and Pawliszyn,[37] one. Additionally, the proportion of alcohols present in the water phase of the current study (42% of the total area of the chromatogram) was expressively higher than that found in fresh cashew apple juice by Garruti et al.,[8] by Bicalho et al.[7] and by Macleod and Troconis.[4] Part of this divergence could be attributed to differences amongst the methodologies used by the mentioned authors to isolate the volatile compounds present in the samples, but part of this difference could also be attributed to a preferential recovery of alcohols in the water phase during juice concentration. In fact, in a study of the recovery of guava volatiles carried out by Jordán et al.,[38] the alcohols present in the water phase represented 65% of the total volatiles (expressed in mg volatiles kg^{-1} essence), while in the fresh purée they only represented 28% of the total volatiles found in the product (expressed in mg volatiles kg^{-1} purée). Similar results were observed in the studies of volatiles recovered during the concentration of passion fruit,[39] banana[40] and kiwi juices.[41] In all the water phases mentioned, the proportion of alcohols almost doubled compared to that present in the fresh juice.

On the other hand, part of the alcohols found in the water phase in the current study may be products of the thermal degradation of other compounds originally present in the fresh cashew apple juice. For instance, Ducruet et al.[42] reported the formation of several alcohols and acids during the storage of strawberries, including 3-methyl-1-butanol, 1-hexanol and butanoic acid, which the authors regarded as degradation products from esters such as hexyl butanoate and 3-methyl butylbutanoate. In citrus juices,[18] excess heat treatment can result in the degradation of esters to alcohols and acids, imparting an off-aroma to the sample described as 'wet dog'.

The proportion of esters identified in the current water phase (21% of the total area of the chromatogram), was significantly lower than that reported for fresh cashew apple juice by Garruti et al.[8] and Bicalho et al.[7] However, all the major esters present in the current water phase, such as ethyl 3-methylbutanoate (3.3% of the total area of the chromatogram), ethyl 2-methylbutanoate (1.0%), and a mixture of ethyl hexanoate and ethyl 2-methyl-2-butenoate (0.7%), were also amongst the most abundant esters reported by the above-mentioned authors. For instance, for Garruti et al.[8] ethyl 3-methylbutanoate was the major ester identified in their sample. Similarly, for Bicalho et al.[7] ethyl 2-hydroxy-4-methylpentanoate was the major ester found in the fresh cashew juice, followed by ethyl hexanoate and ethyl 2-methyl-2-butenoate. In juice concentration, considering the acidic conditions of the juice, excess heating will result in the breaking down of esters to alcohols and acids.[18] Further investigations are needed before concluding that these reactions explain the lower proportion of esters and the higher proportion of alcohols identified in the current water phase, as compared with the results reported by other researchers.[4,5,7–10,37]

Acids were present in moderately high proportions in the water phase analysed in the present study, notably 2-methylbutanoic and 3-methylbutanoic acids (11.6% of the total chromatogram area). However, in most studies carried out with cashew apple juice, acids were minor volatiles.[4,5,7–10,37]

While aldehydes were minor volatile compounds in the water phase analyzed in the present study (1.9% of the total chromatogram area), they were reported as major compounds by Garruti et al.[8] and by Macleod and Troconis[4] in fresh cashew juice. It is possible that part of this divergence is due to differences amongst the methodologies used by the mentioned authors to isolate the volatile compounds present in the samples. It is also possible, however, that part of the aldehydes evaporated from the juice during the concentration process were not efficiently recovered in the water phase.

The proportion of lactones identified in the present water phase was similar to the values reported by most researchers working with fresh cashew apple juice.[5,6–8,10,37]

Aroma volatiles recovered in the water phase

The sensory assessment of the water phase chromatographic effluents revealed the presence of 52 odour-active compounds (Fig. 1). Acids were the class of volatiles causing the highest odour impact in the GC effluents, notably the mixture of 3-methyl-butanoic and 2-methylbutanoic acids (peaks 44 and 45), described as possessing a 'cheesy' odour, perceived at an average intensity of 9.2 on a 10-point intensity scale, and contributed to 26.7% of the total area of the water phase aromagram (Table 4). 2-Methyl-butanoic acid was also the volatile promoting the highest odour impact in the GC effluents of fresh cashew apple juice analysed by Garruti et al.,[8] and by Valim et al.[9] in processed cashew apple juice, where it was described as imparting 'overripe fruit' and 'sweaty' notes to the GC effluents. Overall, although acids represented the class of compounds occupying the highest percentage of the total
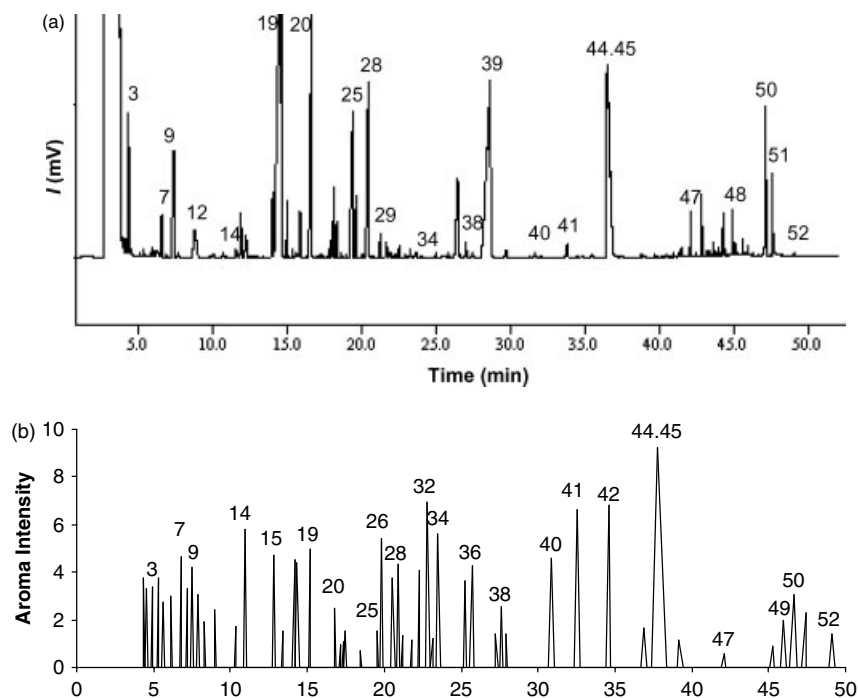
Figure 1. (a) Gas chromatogram and (b) consensus aromagram of cashew water phase isolate showing the positions of some odour-active compounds.

area of the water phase aromagram, this was mostly due to the mixture of 3-methylbutanoic and 2-methylbutanoic acids.

Esters were the second most important class of odour compounds present in the water phase, representing 25% of the total area of the water phase aromagram, a value inferior but comparable to the 36% found in the fresh cashew apple[8] aromagram (Table 4). Most of the esters identified in the water phase isolate were aroma compounds and possessed odour notes described as fruity, sweet and cashew apple-like, notably ethyl 2-hydroxyhexanoate (peak 41), ethyl *trans*-2-butenoate (peak 15), ethyl 2-methylbutanoate (peak 7), ethyl 3-methylbutanoate (peak 9), methyl 2-ethylacrylate (peak 17) and ethyl octanoate (peak 31). Undoubtedly esters were the most important beneficial contributors to the sensory quality of the water phase, notably to the aroma notes described as fruity, sweet and cashew apple-like. Similarly, esters were the most important volatiles associated with the aroma of fresh cashew apple juice analyzed by Garruti *et al.*[8] and by Maciel *et al.*,[5] notably ethyl butanoate, ethyl 2-methylbutanoate, ethyl 3-methylbutanoate and ethyl *trans*-2-butenoate.

The results shown in Table 4 indicate that after the esters alcohols were the class of compounds that most contributed to the desirable aroma notes perceived by the sensory panel in the water phase. Together, alcohols represented 17.2% of the total aromagram area, and were mostly associated with aroma notes described as green grass and fruity. Of the odour-active alcohols identified in the water phase, heptanol, *trans*-3-hexen-1-ol, 3-methyl-1-butanol, 1-octanol and 2-ethyl-1-hexanol imparted the highest odour intensity to the GC effluents. In the cashew apple isolate[8] alcohols represented only 6% of the total aromagram area, and *cis*-3-hexenol alone represented 5% of the total area. In the fresh juice analysed by Garruti *et al.*[8] alcohols represented only 5.6% of the total area of the aromagram, most of this area (5.1%) being due to the odour of *cis*-3-hexen-1-ol.

Finally, aldehydes were the least significant class of aroma volatiles identified in the water phase GC effluents. They represented only 6.4% of the total aromagram area, and were mostly associated with the odour impact of 2-methyl-4-pentenal and *trans*-2-hexenal, the former being described as possessing a desirable green grass and fruity aroma note, and the latter mostly associated with undesirable odour notes (Table 4). In the fresh cashew apple juice studied by Garruti *et al.*,[8] aldehydes showed greater importance as odour volatiles, since they represented 17% of the total aromagram area, mostly related to the odours of hexanal, 2-methyl-2-pentenal, *trans*-2-hexenal and octanal.

Of the ketones and lactones, acetophenone and γ-dodecal-actone were the most significant odour compounds perceived in the GC effluents of the water phase. The former was associated with an undesirable aroma described as 'cheesy' and 'waxy', the latter as possessing a 'cashew' and 'herb' aroma. Together, both compounds represented 6.8% of the total area of the aromagram, suggesting that ketones are not major contributors to the overall aroma of the water phase analysed in the present study. Similar results were reported by Garruti *et al.*[8] for fresh cashew apple juice and by Valim *et al.*[9] for thermally processed cashew juice.

CONCLUSIONS

Unlike previous results reported for fresh cashew apple juice and the fruit,[5,7,8] alcohols, and not esters, were the volatiles present in highest proportions in the water phase. However, esters promoted a greater impact in the water phase odour than the alcohols. After the acids, esters were the most important class of odour compounds present in the water phase. The relatively high proportion of alcohols in the water phase, to the detriment of the presence of esters, is certainly an interesting topic for further investigation. Overall, the results of the present study strongly indicate that further concentration of the recovered esters, either by partial distillation or by alternative technologies

Table 4. Odour intensity and quality of aroma volatiles evaluated in the GC effluents of cashew apple water phase, as well as their relative areas in the aromagram (%) ($n_1 = 5$ judges; $n_2 = 3$ replications)

Peak	Compound	Freq.[a]	Descriptor[b]	I_{max}[c]	%A_{Osme}[d]	%A_{FID}[e]
	Ester				24.66	19.89
1	Ethyl propanoate	13	Fruity, sweet, cashew apple	3.76	0.82	0.12
2	Ethyl 2-methylpropanoate	10	Fruity, sweet, cashew apple	3.29	1.17	0.16
4	Methyl 3-methylbutanoate	14	Fruity, grass	3.76	0.88	0.15
5	Ethyl butanoate	11	Fruity, overripe cashew	2.73	0.52	0.17
7	Ethyl 2-methylbutanoate	14	Fruity, cashew, sweet	4.68	1.76	0.97
9	Ethyl 3-methylbutanoate	14	Cashew apple, sweet	4.21	1.58	3.31
13	Isoamyl acetate	6	Enamel, fruity, banana	1.72	0.43	0.05
15	Ethyl *trans*-2-butenoate	14	Fruity, cashew apple, flower	4.72	1.81	0.04
16	Ethyl 3-methylpentanoate	7	Fruity, grass, cashew apple	1.55	0.53	0.04
17	Methyl 2-ethylacrylate	11	Beetle, grass, sweet, flower	4.15	1.36	tr
21	Ethyl *trans*-3-hexenoate	5	Fruity, flower, cashew apple	0.95	0.12	0.05
24	Ethyl *trans*-2-hexenoate	4	Fruity, sweet	0.69	0.12	0.09
29	Ethyl 3-hydroxy-3-methylbutanoate	5	Fruity, grass, grain, cashew	1.34	0.32	0.24
31	Ethyl octanoate	14	Grain, wet ground, butter	4.08	1.47	tr
35	Methyl 2-hydroxy-3-methylpentanoate	13	Fruity, guava, citric, flower	3.61	1.38	0.03
38	Methyl 2-hydroxy-4-methylpentanoate	11	Fruity, grass, cashew	2.52	0.74	0.34
39	Ethyl 2-hydroxy-4-methylpentanoate	5	Fruity, lemon	1.38	0.29	13.97
41	Ethyl 2-hydroxyhexanoate	15	Cashew, 'pitanga'	6.63	5.29	0.12
43	Ethyl decanoate	6	Cashew, flower, grass	1.68	2.69	tr
46	Ethyl 3-hydroxyhexanoate	5	Grass, fruity	1.16	1.38	0.04
	Alcohol				17.17	36.53
6	2-2-Methyl-3-buten-2-ol	10	Fruity, cooked pineapple	3.00	0.87	0.29
12	2-Methyl-1-propanol	8	Grass, grain	2.39	0.52	1.62
19	3-Methyl-1-butanol	11	Overripe cashew	5.00	1.40	24.03
22	*Trans*-2-Penten-1-ol	5	Grass, mould, fermented	1.09	0.18	0.10
23	4-Methyl-1-pentanol	7	Grass, herb, green fruit	1.50	0.47	0.29
25	Hexanol	5	Grass, sweet, almond oil	1.54	0.47	4.11
26	*Trans*-3-Hexen-1-ol	15	Grass, fruity, perfume, floral	5.43	2.68	0.94
28	*cis*-3-Hexen-1-ol	10	Grass, sweet, fruity	4.31	1.50	4.52
34	Heptanol	13	Cashew, fruity, grass	5.63	2.85	0.14
36	2-Ethyl-1-hexanol	10	Grass, herb, floral	4.29	2.18	0.10
40	1-Octanol	14	Floral, fruity, grass	4.56	4.05	0.39
	Aldehyde				6.38	1.94
10	Hexanal	11	Grass, herb	3.03	1.04	0.11
14	2-Methyl-4-pentenal	15	Grass, fruity, sweet	5.81	2.90	0.12
18	*Trans*-2-Hexenal	11	Pentatomidae bug, grass	4.42	2.22	1.54
33	Furaldehyde	7	Wood, coconut, unpleasant	1.24	0.22	0.17
	Ketone/lactone				9.77	12.88
3	2,3-Butanedione	13	Fermented, cashew, sweet	3.39	0.98	3.30
8	2,3-Pentanedione	11	Fruity, cashew, fermented	3.30	1.19	0.07
20	3-Hydroxy-2-butanone	8	Fruity, herb	2.47	0.76	7.08
42	Acetophenone	13	Cheese, acid, sweet, wax	6.81	2.93	0.38
49	γ-Dodecalactone	8	Cashew, wine, herb	3.06	3.91	2.05
	Acid				35.43	12.32
32	Acetic acid	15	Cooked pineapple, medicine	6.95	4.27	tr
44	3-Methylbutanoic acid +	15	Cheese, foot odour	9.23	26.72	11.63
45	2-methylbutanoic acid					
47	Hexanoic acid	4	Cashew, sweet, grass	0.57	0.31	0.34
48	Nonanoic acid	4	Sweet, fruity	0.86	0.38	0.08
49	Decanoic acid	7	Floral, grass, citric	1.95	2.28	0.27
52	Phenylacetic acid	4	Woody, overripe cashew	1.42	1.47	tr
	Compounds not detected by the FID or not identified by GC–MS				5.23	5.09
11	Peak 11 ND	6	'Cajuina', grain	1.90	0.61	–
27	Peak 27 NI	11	Grass	3.73	1.87	1.05

Table 4. (*Continued*)

Peak	Compound	Freq.[a]	Descriptor[b]	I_{max}[c]	%A_{Osme}[d]	%A_{FID}[e]
30	Peak 30 NI	5	Fruity, cashew, sweet, floral	1.17	0.36	tr
37	Peak 37 NI	6	Plastic, wood, grain	1.38	0.42	2.85
51	Peak 50 NI	7	Grain, beer, cashew	2.29	1.97	1.19

[a] Frequency: number of times that each volatile was perceived in the GC effluents across all judges and repetitions (5 judges, 3 replications).
[b] Descriptors: main descriptors generated by the judges.
[c] Average intensity at the consensual Osmegram (0 = none; 10 = extreme).
[d] Percentage of the total aromagram area.
[e] Percentage of the total chromatogram area.
ND, not detected by FID; NI, not identified.

such as pervaporation, could generate a natural cashew apple water phase or essence with greater quality.

ACKNOWLEDGMENTS

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