Aroma-Relevant Volatile Compounds as Markers for the Sensory Quality of Argan Oil

Bertrand Matthäus,* Anja Bonte, Bernadette Sinning, and Zoubida Charrouf

The aim of the present work is to identify and characterize the most important aroma active compounds of argan oil from unroasted and roasted argan almonds as well as roasted almonds obtained from goat-digested fruits by dynamic headspace GC and GC-olfactometry with aroma dilution analysis to classify samples from the market according to their processing. While fresh ground argan almonds are characterized by only seven aroma active compounds, in argan oil from unroasted and roasted almonds, 22 and 35 aroma active compounds are found, respectively. As a result of the roasting process, 14 aroma active compounds with dilution factors $>64$ are detected in the oil by GC-olfactometry. 17 aroma active compounds show significant differences between the three different argan oil qualities. These compounds are used to differentiate the quality of argan oil from the market.

Practical Application: Argan oil belongs to the high-price oils on the market but sometimes the sensory quality of the oil contradicts the positive image that has been built up for oil by unpleasant cheese-like and fusty sensory attributes. Although some information about the composition of the volatile compounds of cold-pressed argan oil from unroasted and roasted kernels is available, the knowledge about compounds that are typical for the aroma of argan oil is important in order to develop analytical methods for the classification of different argan oil qualities. This reduces the work for a panel group that is often time and labor consuming and sometimes the results are not reliable. The present paper demonstrates which volatile compounds show significant differences between argan oil from unroasted and roasted argan almonds as well as roasted almonds obtained from goat-digested fruits allowing a differentiation of these oils.

1. Introduction

Argan oil becomes more and more popular in Western Europe, not only as oil from unroasted seeds for cosmetics but especially as edible oil from roasted seeds in the high cuisine. Both types of oil are extracted from argan almonds either by an ancestral multistep process or by an oilseed screw press.[1] The fallen ripe fruits are collected between May and August and after sun drying for a few days, the dried peel is removed manually or by a machine. The almonds are extracted from the argan nuts by cracking the nuts between two stones manually and roasted by open fire or indirectly in a gas burner for the production of edible oil. In case of the ancestral multistep process, the almonds are crushed using a millstone. After malaxation for several minutes by hand, the brownish viscous liquid is mixed with water to free the oil in an emulsion. In the more modern method, the almonds are pressed by a screw press, which commonly results in a more effective and reliable processing.[1–3]

Cold pressed edible oils produced by screw pressing and filtration or sedimentation are only defined by the characteristic smell and taste for the seed or fruit from which it is derived.[4] That is the main difference to the refined oils. For the consumer, the sensory characteristics of cold-pressed oils are important for the buying decision. Therefore, the producer of these oils has the duty to produce cold-pressed edible oils with typical taste and smell, and without any sensory defect.

High-quality edible argan oil from sound raw material is characterized by the sensory attributes "roasted" and "nutty," while failure in the processing can result in appearance of atypical attributes such as (Roquefort) "cheese-like" or "fusty."[5] Argan oil from unroasted almonds is characterized by a nutty aroma resulting from the argan fruit while the attribute roasted is developed during roasting. The passage of argan fruits through the intestine of goats results in strongly modified aroma of the oil[6] and the formation of typical off-flavors such as cheese-like and fusty making the oil inedible.[5] The perception of such sensory defects is directly correlated with losses of quality caused by improper raw material (fusty, musty, Roquefort cheese), unsuitable processing during roasting (“burnt”) or inappropriate storage conditions of the oil (“rancid”). Therefore, the sensory assessment is the most
important parameter to evaluate the quality of edible oils and to fulfill the expectations of the consumers. For the sensory evaluation of edible oils, different standard methods are available, such as method DGF-C-II 1 (14) of the German Society for Fat Science (DGF) or AOCS CG 2–83 (8) of the American Oil Chemists’ Society (AOCS) but they are time and labor intensive and the results sometimes have a certain uncertainty.

Profiling and characterization of volatile compounds from edible oils in combination with statistical means seems to be a promising approach to use volatile compounds for the differentiation of oil qualities and to support the sensory evaluation. Especially for virgin extra olive oil, several studies have been published showing that sensory defects are correlated with the presence of certain volatile compounds. (9–12) Investigations on the profile of volatile compounds have been carried out for other edible oils as well to find key compounds to support sensory evaluation. (4,13)

In the case of argan oil, only little information about the composition of the volatile compounds is available. Charrouf et al. (9) analyzed the influence of goat digestion and kernel roasting on volatile compounds of argan oil by gas chromatography–mass spectrometry (GC–MS) and olfactometry. They mainly found aldehydes and ketones formed from autoxidation of linoleic acid. In addition, pyrazines from roasting of the kernels were described. El Monfalouti et al. (15) investigated the effect of roasting at 110 °C for up to 25 min on the composition of volatile compounds by SPME and GC–MS. It was shown that roasting induces the formation of compounds resulting from Strecker degradation, lipid oxidation, and Maillard reaction. Zahir et al. (16) isolated volatile compounds from argan oil by dynamic headspace extraction followed by GC–MS and olfactometry. In argan oil from unroasted kernels, a limited number of volatiles were found while argan oil from roasted almonds showed degradation products of Maillard reaction, lipid oxidation, and sugar degradation with higher levels of pyrazines, aldehydes, and ketones in semi-mechanical processed oils. In a recent paper, Gracka et al. (17) identified 2-methylbutanal, acetic acid, pentanal, hexanal, 2,5-dimethylpyrazine, methylpyrazine, 2,3-butanediol, and 1-methyl-1H-pyrrole as volatile markers to detectable for the typical attributes. (18) All tasters of the panel were trained in different characterization of the most important aroma active compounds of argan oil from unroasted and roasted almonds as well as roasted almonds obtained from goat-digested fruits to classify oils during storage. For the first time, they used statistical multivariate analysis to differentiate between raw and roasted argan oils of various degrees of oxidation and also identified volatile compounds that are responsible for the unique flavor of argan oil from roasted almonds.

The aim of the present work was the identification and characterization of the most important aroma active compounds of argan oil from unroasted and roasted almonds as well as roasted almonds obtained from goat-digested fruits to classify samples from the market according to their processing. The results should provide necessary information on the main volatiles that are responsible for sensory differences between different argan oils from different processing usable for quality control.

2. Experimental Section

2.1. Materials

2.1.1. Reference oils

Two argan oils from unroasted (mechanical extracted) almonds, two argan oils from roasted (mechanical extracted and hand-pressed, respectively) almonds (La Cooperative Taitmatine, Taroudant, Morocco and Tighanimine Filahia, Province Agadir, Morocco), and one argan oil from roasted almonds obtained from goat-digested fruits (purchased from the Tiout Market, Taroudant, Morocco).

Fresh argan kernels were obtained from the La Cooperative Taitmatine, Taroudant, Morocco. For GC-olfactometry (GC-O), the fresh argan almonds were crushed and 1 g of the material was filled into a headspace vial.

Four virgin argan oils from unroasted almonds, seven cold-pressed argan oils from roasted almonds obtained by screw-pressing, and two hand-pressed argan oils were purchased from the German market.

The following 53 compounds were used as standards and integrated into a MeltDB reference list for automated peak identification:

- Acetaldehyde, acetic acid, acetic acid amyl ester, 2,3-butanediol, 2,3-butanediole, butanenitrile, butanoic acid, butanoic acid methyl ester, 1-butanol, 2-butenenitrile, γ-butyrolactone, ethanol, heptanenitrile, 1-heptanol, γ-hexalactone, hexanal, hexanenitrile, 3-hydroxy-2-butanone, 2-isobutyl-3-methoxypyrazine, isopropyl isothiocyanate, isopropyl-3-methoxyprazine, 1-isothiocyanatobutane, 4-isothiocyanato-1-butenone, 1-isothiocyanatoheptane, n-limonene, 3-methylbutan-2-methyl-1-butanol, 2,4-nonadienal, nonanal, γ-octalactone, octanal, 2-octal, 1-octen-3-ol, 4-pentenoic acid ethyl ester, α-phellandrene, 2-phenylethanol, α-piene, β-piene, propanoic acid 2-methylthyl ester, 1-propanol, thiocyanic acid methyl ester, toluene, and γ-valerolactone (Sigma–Aldrich Chemie GmbH, Taufkirchen, Germany); benzoic acid ethyl ester (Carl Roth GmbH & Co. KG, Karlsruhe, Germany), 2,4-decadienal, 2-methylbutanoic acid, 3-methylbutanoic acid, and 2-methylpropanal (Merck IGaA, Darmstadt, Germany); (2Z)-4-heptenal, 2,6-nonadienal, 1-octen-3-one (H+R AG, Salzberg, Germany); pentanoic acid (Alfa Aesar, Kandel, Germany).

2.2. Sensory Evaluation

The sensory evaluation of the cold-pressed argan oils was carried out according to method DGF C-II 1 (14) with four trained tasters. (7,18) All tasters of the panel were trained in different characteristic attributes of cold-pressed argan oil flavors and they were familiar with the main defects of these oils such as “cheese-like” (Roquefort cheese), “rancid,” “wood-like,” “bitter,” “burnt,” “musty,” “yeast-like,” “fusty,” and others defined in the standard method. In brief, 15 ± 1 mL of the samples were weighed into a blue colored glass and then covered by a lid. Afterwards the sample was first smelled and then tasted at room temperature. The flavor and taste of the oils were characterized according to a sensory description form, with a scoring system for the typical attributes (nutty, roasty) from 0 (not perceptible) to 5 (very intensively perceptible) as well as detectable or not detectable for the atypical attributes. (18)
2.3. Dynamic Headspace GC–MS

All samples were analyzed in two technical replicates. Analysis was carried out according to method DGF-C-VI 20 (15) and performed as described in Bonte et al. (14). A mix of six alkanes (pentane, heptane, octane, nonane, undecane, and tridecane), each in a concentration of 1 mg kg⁻¹, was added to the 200 mg oil samples, to create the retention index (RI). Volatiles were purged from the oil samples by a PTA 3000 dynamic headspace system (IMT, Vohenstrauß, Germany). After accumulation for 20 min at an online Tenax trap at −65 °C volatiles were transferred to the GC system by 10 min desorption at 200 °C. Separation was carried out with a Trace 1300 Series GC (Thermo Scientific, Darmstadt, Germany) on a CPSil19 fused silica capillary column (14% cyanopropyl-phenyl ± 86% dimethylpolysiloxane, 60 m, 0.32 mm ID, 1 µm film thickness). Separated volatiles were detected after electron ionization in positive mode at an ISQ Mass spectrometer (Thermo Scientific). Before each new sequence a blank run only consisting of air was carried out to make sure that no contamination from one sequence to the next occurred. Chromatograms were converted to netCDF-file format and uploaded to the MeltDB-Software.

2.4. GC–FID-Olfactometry

The aroma profile of oils from unroasted and roasted argan almonds as well as almonds obtained from goat-digested fruits was obtained by GC-olfactometry on a GC–FID (Hewlett-Packard 5890 Series II, Waldbronn, Germany) with four trained tasters. In brief, 3.0 g of oil was transferred into a 20 mL headspace vial before dynamic headspace analysis was started as described before.

For each sample, four test persons listed the retention time, the aroma description and the intensity of all odor perceptions. These lists were compared with the GC–MS chromatograms of the same sample and the odor impressions were assigned to the appropriate peaks. Volatile compounds were declared as aroma-active, if they were detected by at least three test persons.

An aroma extract dilution analysis was carried out by olfactometry of decreasing amounts of argan oil in a 20 mL headspace vial starting with dilution level 1 (6 g sample oil in the headspace vial) up to level 1024 (5.85 mg sample oil in the headspace vial). The volatile compounds of each level were characterized by three test persons and aroma active compounds were only considered when perceived by at least two from three persons. For each aroma compound identified, a flavor dilution (FD) factor was calculated corresponding to the lowest dilution at which the compound was still perceived.

2.5. Data Analysis with the MeltDB Software Platform

MeltDB is a web-based platform providing the storage, organization, and annotation of large data sets (16). Integrated algorithms for multiple profiling allow peak detection and integration as well as considering non-identified compounds (TAGs) into data analysis if they occur in 80% of all chromatograms of an experiment or in one chromatogram group. These TAGs were labeled with the characteristic mass and the mean retention time. Peaks were identified by comparison of retention time, mass spectra, and retention indices of reference compounds analyzed under the same conditions. Additionally, mass spectra information of peaks was compared with the NIST (National Institute of Standards and Technology) 2008 database. The obtained information allows an identification of differences, and mutual interferences of compounds from samples with characteristic features by means of multivariate methods (principle component analysis (PCA), analysis of variance (ANOVA), Heatmap). In addition, marker compounds can be identified responsible for the specific sensory attributes in argan oil samples of different types of processing.

2.6. Statistical Evaluation

With PCA and hierarchical cluster analysis (Ward method), differences between the various qualities of argan oil were revealed on basis of the peak areas of all detected compounds or of selected compounds with statistically significant differences (one-way ANOVA, \( p = 0.05 \)) between all three types of processing of argan oil. The data were evaluated using the statistical software JMP (SAS Institute Inc.). Each method was carried out in triplicate for each sample.

3. Results and Discussion

The current work followed a stepwise approach. Starting from the sensory evaluation of the different types of argan oil (reference oils) via analyzing and characterizing the volatile compounds by dynamic headspace-GC–MS followed by the identification of statistically significant marker substances for the discrimination of oils from different types of processing and quality levels. Finally, these identified compounds were applied to different oils from the German market to verify their suitability as marker substances.

3.1. Sensory Evaluation

One of the most important characteristic features of argan oil from unroasted and roasted almonds is the sensory evaluation. The sensory quality should meet the expectations of the consumers. In the current investigation, the sensory quality of three different types of argan oil (oil from unroasted, roasted, and roasted, goat-digested almonds) was evaluated. These oils were used as reference oils for the following identification and characterization of the most important volatile aroma compounds. To be sure that these samples were typical representatives of their quality class, the sensory evaluation of the samples was necessary. In addition, the sensory quality of samples from the German market was evaluated to classify them into the three groups of oil quality.

The sensory evaluation of the oils was done using the sensory descriptions mentioned in standard method DGF-C-II 1 (14), with the typical attributes “nutty” and “roasty” found in oils from sound raw material, and with atypical attributes such as
of the “cheese-like” attribute in some cold-pressed argan oils is the use of almonds from goat-digested argan fruits for argan oil production. After passing the intestinal tract of goats almonds take on a typical “cheese-like” smell that is perceivable in the resulting oils in a much stronger intensity than in oils affected by oxidation.

3.2. Dynamic Headspace GC

The characteristic smell and taste of edible oils is often due to a composition of volatile compounds with a high aroma-activity at low concentrations. Therefore, a method working at a high sensitivity level is necessary to get as many of the volatile compounds even at a low concentration level as possible. In case of the profiling of volatile compounds from edible oils, the dynamic-headspace extraction according to method DGF-C-VI 20 (15) emerged as a good compromise with regard to selectivity and sensitivity. Elmore et al. (23) showed that for straightforward analysis of major volatile components solid phase micro extraction (SPME) would be the method of choice but for trace analysis it would appear that only dynamic headspace trapping is suitable.

Results of the analysis of the aroma active, volatile compounds extracted from different types of argan oil by dynamic-headspace analysis are shown in Table 1. In fresh almonds, only crushed and directly measured merely seven aroma active compounds were detected, whereas in oil from unroasted almonds 41 compounds could be found. This shows that processing strongly accelerates the formation of volatile compounds. During the pressing process, cell walls break down and enzymes come into contact with their appropriate substrates. In addition, the passage of the disrupted material through the screw press takes some time resulting in the formation of degradation products from fatty acids and other constituents. Thus, processing results in a wide range of compound classes, such as aldehydes, alcohols, ketones, acids, esters, sulfur compounds, terpenes, furans, and furanones as well as further aromatic compounds in oil from unroasted almonds. This differences to Zaher et al. (16) who mainly found alcohols, aldehydes, and ketones may be due to the use of different raw material. El Monfalouti et al. (15) also found a wide range of compound classes in argan oil from roasted almonds while, as a result of roasting and roasting time, only the amount of these compounds increased but not the number of compounds.

In the current work, the number of volatile compounds in oil from roasted almonds further increased to a number of 66, resulting from the formation of Maillard reaction products, such as pyrazines that were not found in oil from unroasted almonds. The highest number of volatile compounds was found in oil from roasted, goat-digested almonds, in total 76, however, several compounds could not be identified yet.

While El Monfalouti et al. (15) showed that the amount of hexanal increased with the roasting time no significant differences could be detected in the three classes of oil quality in the current work. However, in contrast to the work of El Monfalouti et al. almonds were only subjected to a gentle roasting process in this study. This is assumed as reason for the differences since in the work of El Monfalouti et al. also no significant change in the amount of hexanal could be observed in the first 15 min of roasting.
Table 1. Volatile aroma active compounds extracted from different qualities of argan oil.

| Compound class | Number | Compound | RI GC–MS | Rt GC–MS | Perception | nRA | RA | GdA | Fresh almond | ID | Reference | nRA | RA | GdA |
|----------------|--------|----------|----------|----------|------------|-----|----|-----|--------------|----|-----------|-----|----|-----|
| Pyrazines      | 16     | Pyrazine | 827      | 27.3–27.4 | Sweaty, musty | *   | *  | FD<64 | –            | MS |           |     |     | B   |
|                | 32     | 2,5-Dimethylpyrazine; | 999      | 38.16–38.33 | Nutty, chocolate, musty, herbaceous | *   | *  | FD256 | –            | MS |           | C   | B  | A   |
|                | 34     | Ethylpyrazine | 1005     | 39.10–39.3 | Roasted/burnt, cheese-like | *   | *  | FD<64 | –            | MS | [29]      | C   | B  | A   |
|                | 35     | 2,3-Dimethylpyrazine | 1011     | 39.3–39.41 | Nutty, roasted, coffee | n.d. |     | FD<64 | –            | MS | [15]      | C   | B  | A   |
|                | 50     | 2-Ethyl-5-methylpyrazine | 1084     | 44.2–44.32 | Alcohol, sweet | n.d. |     | FD<64 | *            | MS | [35,29]   | C   | B  | A   |
|                | 59     | 2-Ethyl3,5-dimethylpyrazine | 1158     | 48.5–48.59 | Mildewed, popcorn, cheese-like, mildewed | n.d. |     | FD<64 | –            | MS | [35,29,30] | C   | B  | A   |
|                | 69     | 3,5-Dimethyl-2-methylpyrazine; 3,5-diethyl-2-methylpyrazine | 1234     | 53.1–53.34 | Roasted almonds, popcorn | n.d. |     | *    | FD<64 | –            | MS |           | C   | B  | A   |
| Aldehydes      | 1      | Acetaldehyde | <500     | 7.82–8.02 | Sweet, alcoholic | FDF<64 | FDF<64 | FDF<64 | #            | MS | Ref [30] | C   | B  | A   |
|                | 5      | Propanal    | 548      | 10.38–10.50 | Solvent-like, green | *   | *  | FDF<64 | –            | –  |           | A   | A  | A   |
|                | 6      | 2-Methylpropanol | 609      | 13.73–14.3 | Chocolate, slightly cheese-like | *   | FDF<64 | FDF<64 | –            | MS | Ref [30] | C   | A  | B   |
|                | 11     | 3-Methylbutanal | 734      | 20.58–21.09 | Chocolate, sweet, buttery | FDF<64 | FDF256 | FDF<64 | –            | MS | Ref [29,30] | C   | B  | A   |
|                | 24     | Hexanal     | 884      | 31.13–31.1 | Green, grassy | FDF128 | FDF<64 | FDF<64 | #            | MS | Ref [35,29,30] | A   | A  | A   |
|                | 51     | Octanal     | 1092     | 44.31–44.78 | Sweet, orange, biting, fustig, soapy | FDF<64 | *    | FDF<64 | –            | MS | Ref [29,30] | C   | B  | A   |
|                | 58     | 1-Methylpyrrole-2-carbaldehyde | 1153     | 48.3–48.49 | Mildewed, musty, stinking, earthy | *    | FDF<64 | *    | –            | MS |           | B   | B  | A   |
|                | 63     | Nonanal     | 1199     | 50.4–50.99 | Old fat, soapy, popcorn, orange-like | FDF64 | FDF<64 | *    | –            | MS | Ref [6,15] | B   | B  | A   |
|                | 68     | 1-Hydropyrrole-2-carbaldehyde | 1227     | 52.67–53   | Popcorn, burnt | n.d. | (*)  | FD256 | –            | MS | [15]      | B   | B  | A   |
| Alcohol        | 22     | 1-Pentanol  | 874      | 30.44–30.62 | Musty, beer, slightly biting, herbaceous, burnt | *   | *  | FD<64 | –            | MS | [15]      | C   | A  | B   |
|                | 27     | 3-Methylbutan-1-ol | 943      | 35.03–35.10 | Roasted, slightly burnt, earthy, cacao | *   | *  | FD<64 | –            | MS |           | A   | A  | B   |
|                | 38     | 2-Furanmethanol | 1018     | 39.9–40.36 | Popcorn, green, biting, almond, nutty | *    | FDF128 | FDF128 | –            | MS | [15]      | B   | B  | A   |
| Ketones        | 7      | 2,3-Butanedione | 681      | 16.81–17.3 | Vanilla, buttery | FDF<64 | FDF<64 | FDF<64 | –            | MS | Ref [29,30] | B   | A  | A   |
|                | 28     | 2-Hydroxypentan-3-one | 949      | 35.17–35.5 | | n.d. | *    | FDF<64 | –            | MS |           | C   | A  | B   |
|                | 48     | 1-Octen-3-one | 1068     | 42.98–43.40 | Mushrooms | FDF1024 | FDF1024 | FDF1024 | #            | MS | Ref [6,29] | A   | A  | A   |

(Continued)
| Compound class | Number | Compound                  | RI GC–MS       | Rt GC–O       | Perception                | nRA | RA | GdA | Fresh almond | ID       | Reference          | nRA | RA | GdA |
|----------------|--------|---------------------------|----------------|---------------|---------------------------|-----|----|-----|--------------|---------|---------------------|-----|----|-----|
| Furans         | 12     | 2-Ethenylfuran            | 782            | 23.29–23.43   | Very spicy, green         |     |    |     |              |         | FD<64               | B   | B | A  |
| Acids          | 14     | Acetic acid               | 787–799        | 24.31–24.9    | Biting, acetic           | FD<64| FD<64| #   | MS, Ref [29] | A      | B, AB               |     |    |     |
|                | 30     | Butanoic acid             | 956            | 35.8–36.35    | Biting, spicy            |     |    |     |              |         | FD<64               |     |    |     |
|                | 36     | 3-Methylbutanoic acid     | 1010–1015      | 26.94–27.02   | Cheese-like, sweaty      |     |    |     |              |         | FD128               |     |    |     |
|                | 37     | 2-Methylbutanoic acid     | 1010–1016      | 26.94–27.02   | Cheese-like, sweet       | FD128| FD128| n.d.| MS, Ref [29] | A      | AB, B               |     |    |     |
| Sulphur        | 2      | Methanethiol              | <500           | 8.21–8.33     | Herbaceous, earthy, musty|     |    |     |              |         | FD<64               | A   | B | AB |
|                | 25     | 4-Methylthiazole          | 904            | 32.19–32.29   | Musty, potato-like,       | n.d.|    |     |              |         | FD<64               | B   | B | A  |
|                | 45     | 2,4-Dimethyl-2-thiazoline| 1053           | 42.24–42.3    | Potato, spicy, musty,     | n.d.|    |     |              |         | FD<64               | B   | B | A  |
| Esters         | 9      | Isopropyl acetate         | 723            | 19.95–20.06   | Chocolate, cheese-like,   |     |    |     |              |         | FD<64               | A   | A | B  |
|                | 20     | Ethyl butanoate           | 861            | 29.27–29.5    | Roasted, sweet, fruity,   |     |    |     |              |         | FD<64               | B   | B | A  |
| Terpenes       | 47     | α-Limonene                | 1063           | 42.82–43.06   | Rapseed, potato-like,      |     |    |     |              |         | FD256               | B   | B | A  |
| Furans and     | 44     | 1-(2-Furanyl)ethane      | 1049           | 41.81–42.2    | Butter, rubber, slightly  |     |    |     |              |         | FD<64               | B   | B | A  |
| Furanones      | 60     | 2-Methyl-2H-furan-5-one   | 1163           | 48.49–48.8    | Mushroom, earthy,         |     |    |     |              |         | FD<64               | B   | A | A  |
| Aromatic       | 64     | Phenol                    | 1213           | 51.42–51.7    | Spicy, popcorn, earthy,   |     |    |     |              |         | FD<64               | A   | A | A  |
| compounds      | 76     | 4-Methylphenol            | 1296           | 56.4–56.6     | Goat, slurry              | n.d.|    |     |              |         | FD128               | B   | B | A  |
|                | 77     | 3-Methylphenol            | 1298           | 56.6–56.87    | Biting, stable smell      |     |    |     |              |         | FD128               | B   | B | A  |
| Ether          | 3      | Ethylether                | 518            | 9.91–9.94     | Alcoholic, biting         |     |    |     |              |         | *                   | A   | A | A  |
| Others         | 15     | 2,4,5-Trimethyl-1,3-dioxolane | 806 | 25.93–26.19 | Glue-like, fruity, mushroom-like |     |    |     |              |         | FD<64, FD<64 | A   | A | A  |
|                | 18     | 1-Methyl-1H-pyrole       | 833            | 27.5–27.61    | Glue-like, vanilla, onion |     |    |     |              |         | FD<64, FD<64 | B   | B | A  |
|                | 53     | Dihydro-3-(2H)-thiophenone | 1098         | 45.02–45.19  | Earthy, straw-like, spicy, | n.d.|    |     |              |         | FD<64               | B   | B | A  |
|                | 78     | 2,4-Dimethyl-2-oxazoline-4-methanol | 1308 | 57.1–57.2 | Pungent, goat              | n.d.|    |     |              |         | FD<64               | B   | B | A  |

(Continued)
Table 1. Continued.

| Compound class | Number | Compound | RI GC–MS | Rt GC–O | Perception | nRA | RA | GdA | Fresh almond |
|----------------|--------|----------|---------|--------|------------|-----|-----|-----|-------------|
| TAGs           | 13     | TAG 936.6s 57 m/z | 783 | 23.7–23.97 | Caramel, alcoholic, earthy, cheese-like, buttery, | * | FD<64 | FD<64 | – | B | B | A |
| 17             | TAG 1110.0s 74 m/z | 830 | 27.5–27.63 | Chocolate, acetic, pungent, garlic | n.d. | * | FD<64 | – | n.d. | A | A | A |
| 19             | TAG 1156.8s 55 m/z | 842 | 27.94–28.1 | Chocolate, nutmeg | FDC64 | * | * | – | B | A | B |
| 21             | TAG 1217.5s 55 m/z | 861–867 | 29.62–19.71 | Glue, burnt, sweet | FD<64 | FD64 | * | – | n.d. | B | B | A |
|                | Peak overlay by acetoin 43 m/z // 45 m/z | 916 | 32.41–32.53 | Potato-like, starchy | compound was only olfactometricaly detected in argan almonds | n.d. | n.d. | FDS12 | – | MS | B | B | A |
| 39             | TAG 1844.4s 97 m/z | 1026 | 40.13–40.18 | Popcorn, buttery, toasted | * | FD<64 | * | – | A | A | A |
| 33             | TAG 1746.6s 67 m/z | 1000 | 38.66–38.9 | Glue, sweet, soapy, earthy, | n.d. | FDS12 | FD<64 | – | C | B | A |
| 54             | TAG 2155.8; 120 m/z | 1113 | 45.24–45.57 | Popcorn, roasted, biting, slightly burnt, sweet, soapy | n.d. | FD<64 | FD256 | – | MS | B | B | A |
|                | Peak overlay by acetoin 43 m/z // 45 m/z | 1120 | 46.54–46.8 | Camomile tea, earthy, biting, clue | n.d. | n.d. | FDS12 | – | MS | B | B | A |
| 56             | TAG 2251.4s; 95 m/z | 1143 | 47.63–47.88 | Goat shed | n.d. | n.d. | FD1024 | – | MS | B | B | A |
| 57             | TAG 2273.9s; 86m/z | 1150 | 48.02–48.4 | Pungent, green, biting | n.d. | n.d. | FD1024 | – | MS | B | B | A |
| 62             | TAG 2423.5s; 69 m/z | 1196 | 50.6–50.9 | Flowerly, rancid, cow shed, biting, soapy | n.d. | FDC64 | – | – | MS | C | B | A |
| 65             | TAG 2481.6s; 80 m/z | 1214 | 51.7–51.76 | Pungent, sweet, earthy, musty, roasted | n.d. | * | FD<64 | – | MS | C | B | A |
| 66             | TAG 2492.0s; 83 m/z | 1217 | 52.05–52.21 | Paint, sweet, orange-like | (‘) | (‘) | FD4096 | – | MS | B | B | A |
| 70             | TAG 2520.6s; 119 m/z | 1235 | 53.21–53.42 | Popcorn, coffee | n.d. | (‘) | FD64 | – | MS | B | B | A |
| 71             | TAG 2568.6s; 141 m/z | 1241 | 53.51–53.6 | Roasted almonds, buttery | n.d. | n.d. | FD<64 | – | MS | B | B | A |
| 72             | TAG 2578.1s; 118 m/z | 1244 | 53.58–53.72 | Cotton candy, popcorn, herbaceous | n.d. | FDC64 | – | – | MS | C | B | A |
| 73             | TAG 2646.7s; 129 m/z | 1265 | 54.6–54.77 | Popcorn, earthy, slightly spicy, burnt | n.d. | n.d. | FD256 | – | MS | B | B | A |
| 74             | TAG 2673.6s; 157 m/z | 1273 | 55.4–55.56 | Roasted almonds, biting | n.d. | n.d. | FD256 | – | B | B | A |
| 75             | TAG 2694.3s; 95 m/z | 1293 | 55.6–55.91 | Nutty, almond, pea-like (green) | FD<64 | FD256 | FD128 | # | MS | A | A | A |
| 79             | TAG 2791.6s; 80 m/z | 1309 | 57.2–57.4 | Stable smell | n.d. | * | FD64 | – | C | B | A |
| 80             | TAG 2793.2s; 100 m/z | 1310 | 57.47–57.53 | Stable smell | n.d. | n.d. | FD256 | – | B | B | A |
| 81             | TAG 2802.2s; 134m/z | 1313 | 57.6–57.8 | Stable smell | n.d. | * | FD128 | – | MS | B | B | A |
| 82             | TAG 2828.1s; 81 m/z | 1321 | 58.04–58.23 | Goat | n.d. | * | FD256 | – | MS | B | B | A |
| 83             | TAG 2879.5s; 108 m/z | 1337 | 58.7–58.85 | Metallic, mustily | n.d. | n.d. | FD256 | – | B | B | A |
| 84             | TAG 2931.0s; 109 m/z | 1353 | 59.6–59.57 | Sweet, almond, lemony | n.d. | FD<64 | FD<64 | – | B | B | A |

(Continued)
| Compound class | Number | Compound   | RI GC–MS | Rt GC-O | Perception                                                                 | nRA | RA  | GdA | Fresh almond | ID   | Reference | nRA | RA  | GdA |
|----------------|--------|------------|----------|---------|-----------------------------------------------------------------------------|-----|-----|-----|--------------|------|------------|-----|-----|-----|
| unknown        | 8      | Unknown    | 77       | 19.4-19.95 | Spicy, onion, biting                                                        | –   | –   | FD<64 | –            | n.d. |            |     |     |     |
| 10             | Unknown| 724        | 20.2-20.46 | Sweaty, cheese-like, green                                                  | –   | –   | FD<64 | –            | n.d. |            |     |     |     |
| 23             | Unknown| 878        | 30.7-30.92 | Spicy, herbs, green, biting, sweet,                                       | –   | –   | FD<64 | –            | n.d. |            |     |     |     |
| 26             | Unknown| 904        | 32.43-32.65 | Fruit gum                                                               | FD 1024|     | FD64 | #            | n.d. |            |     |     |     |
| 31             | Unknown| 983        | 37.06-37.3 | Earthy, biting, roasted, herbaceous, almond-like                         | –   | –   | FD64  | –            | n.d. |            |     |     |     |
| 40             | Unknown| 1029       | 40.3-40.43 | Rapeseed, strong animal smell roasted                                    | –   | –   | FD128 | –            | n.d. |            |     |     |     |
| 41             | Unknown| 1037       | 40.6-40.89 | Bisquit, slightly dusty, roasted                                          | –   | –   | FD256 | –            | n.d. |            |     |     |     |
| 42             | Unknown| 1035       | 40.70-40.95 | Fruity, burnt, biting, wood-like, sweaty, rubber, popcorn               | –   | –   | FD256 | –            | n.d. |            |     |     |     |
| 43             | Unknown| 1045       | 41.98-42.1 | Rancid, potato-like                                                        | –   | –   | FD256 | –            | n.d. |            |     |     |     |
| 46             | Unknown| 1057       | 42.55-42.74 | Green, earthy, roasted, chocolate                                       | –   | –   | FD256 | –            | n.d. |            |     |     |     |
| 52             | Unknown| 1094       | 44.46-44.7 | Sweety, orange, lemony, soapy                                             | –   | –   | FD128 | –            | n.d. |            |     |     |     |
| 67             | Unknown| 1218       | 52.08-52.15 | Fusty, musty                                                               | FD128|     | –    | –            | n.d. |            |     |     |     |

n.d., not detected; MS, mass spectrum; *olfactometrically detected; **compound was not perceived olfactometrically, but has been detected by MS; ***compound was not perceived olfactometrically, but has been detected by MS only in some reference oils; ****not olfactometrically detected, no detection by MS; Different characters indicate significant differences of the mean values; A, highest mean value; C, lowest mean value; bold characters indicate compounds with significant differences according to all three groups of oil qualities: nRA, oil from unroasted almonds; RA, oil from roasted almonds; GdA, oil from roasted, goat-digested almonds; ID, method of identification; FD, dilution factor; RT, retention time; RI, retention index; Ref, identified by reference compound; MS, identified by MS spectrum.
Table 1 shows that not only the highest number of aroma active compounds was present in oil from roasted, goat-digested almonds, but also significant higher amounts of these compounds in comparison to the other oil qualities. This means that the sensory quality of argan oil is determined by both, the presence of individual aroma active compounds as well as the amount of these compounds. This phenomenon was also found for virgin rapeseed oil when the composition of aroma active compounds in virgin rapeseed oil of bad and good sensory quality was very similar, but significant differences occurred in the amount of individual compounds explaining the different sensory qualities.\cite{14}

### 3.3. GC-FID-Olfactometry and GC-MS Analysis

Three reference oils from each of the categories (roasted and unroasted almonds as well as almonds obtained from goat-digested fruits) were used for olfactometry analysis. In addition, freshly crushed almonds were analyzed to get information about the initial composition of volatile compounds from argan almonds.

According to the sensory evaluation, the reference oils were typical representatives of their quality class with respect to the smell. In total, 43 aroma-active compounds could be identified and further 25 compounds were detected as aroma-active TAGs. In freshly crushed argan almonds, the four compounds acetaldehyde, acetic acid, hexanal, and 1-octen-3-one were detected as aroma active by olfactometry. In addition, an odor impression occurred at the not identified compounds TAG 2694.3 s 95 m/z and TAG 1488.0s 77 m/z. TAG 1488.0s 77 m/z was only identified in crushed argan almonds with a strong olfactory impression as “potatoes” and “starchy,” but not in the oils. Another unknown compound (26) was identified as aroma active (“fruit gum”) in the crushed almonds but also in oil from roasted (FD 1024), unroasted (FD 512), and goat digested (FD 64) almonds. But due to its low concentration no reliable and meaningful MS spectrum could be obtained from this compound. 1-Octen-3-one also showed a very strong aroma activity in the three different types of oil (FD 1024), but it was also not possible to detect the compound by GC-MS. Nevertheless, the identification was carried out by comparison of the retention time and odor impression to an analyzed reference compound.

Hexanal and 1-octen-3-one are two main oxidation products of linoleic acid,\cite{24} which is known as one of the major fatty acids of argan oil. During crushing the almonds cell walls were destroyed and oil came into contact with air resulting in small amounts of both compounds formed by oxidation. 1-Octen-3-one is characterized by a spicy, fatty, and nutty smell.\cite{24}

The main classes of compounds detected in oil from unroasted and roasted almonds were aldehydes, ketones, alcohols, pyrazines, and acids in varying intensities. In the largest class, aldehydes, only for hexanal a stronger intensity was perceivable in the oil from unroasted almonds in comparison to the oil from roasted almonds. Oil from roasted almonds was characterized by the occurrence of Maillard reaction products such as pyrazines or furans that are formed during the reaction of reducing sugars and amino acids. This reaction results in a large number of different aroma active compounds contributing to the nutty and roasty sensory attributes of argan oil from roasted almonds.

In contrast to fresh crushed almonds in argan oil from unroasted almonds 41 and in argan oil from roasted almonds, 62 aroma active compounds were detected by GC-olfactometry (Table 1). In argan oil from roasted almonds, several compounds with a perception as “nutty” or “roasted” were found exclusively. Some of these compounds were only detectable with dilution factors below 64 in the aroma profile. 2,3-dimethylpyrazine (no. 35; “nutty,” “roasted”), TAG 2155.8 120 m/z (no. 54; “popcorn,” “roasted”), 2-ethyl-3,5-dimethylpyrazine (no. 59; “popcorn,” “cheese-like”), while others had dilution factors between 64 and 256: unknown compound (no. 41; “biscuit,” “fusty,” “roasted,” FD 256), TAG 2694.3s 95 m/z (No. 75; “nutty,” “green,” “pea-like,” FD 256), 2-furanmethanol (no. 38; “popcorn,” “green,” “almond,” “nutty,” FD 128), and TAG 2578.1s 118 m/z (no. 72; “cotton candy,” “popcorn,” FD 64).

Gracka et al.\cite{15} used an extract obtained by SAFE extraction for GC-O analysis, in comparison to dynamic head-space GC-O in the current work. However, they described similar results for compounds that have a great influence on the aroma of argan oil, with aldehydes such as butanal and hexanal as volatile compounds mainly determine the aroma of argan oil from unroasted almonds, while especially pyrazines such as 3-isopropyl-2-methoxypyrazine and 2-ethyl-3,5-dimethylpyrazine with FD values of 1024 were responsible for the aroma of oil from roasted almonds. Zaher\cite{16} also identified different pyrazine derivatives (2-ethyl-5-methylpyrazine, 2-ethyl-6-methylpyrazine, 2-ethyl-5,2-dimethylpyrazine, and 3-ethyl-2,5-dimethylpyrazine) with a strong contribution to the aroma of argan oil from roasted almonds by GC-O. Even if in the current work other pyrazine derivatives were identified contributing to the aroma of argan oil from roasted almonds, the comparison of the results of GC-O analysis of different groups show that these groups of compounds are very important for the aroma of argan oil from roasted almonds.

Most aroma active compounds (75) were found in argan oil from almonds obtained from goat-digested fruits. Additionally two pyrazines and other Maillard reaction products as well as eight aroma active compounds were identified exclusively in this argan oil: TAG 2273.9s 86 m/z (no. 57; “biting,” “green”; FD 1024), 4-methylphenol (no. 76; “goat-like”; FD 1024), 3-methylphenol (no. 77; “stable smell,” “biting”; FD 256), TAG 2791.6s 100 m/z (no. 79; “stable smell”; FD 64), TAG 2793.2s 100 m/z (no. 80; “stable smell”; FD 256), TAG 2828.1s 81 m/z (no. 82; “goat”; FD 256), and TAG 2879.5s 108 m/z (no. 83; “metallic,” “mustily”; FD 256). Further compounds typical for argan oil from roasted almonds obtained from goat-digested fruits are 2,4-dimethyl-2-thiazoline (no. 45; “potato-like,” “spicy”; FD 64), TAG 2646.7s 129 m/z (no. 73; “popcorn,” “slightly spicy,” “earthy”; FD 256), and TAG 2673.6s 157 m/z (no. 74; “biting,” “roasted almonds”; FD 256).

### 3.4. Principal Component Analysis

PCA is a tool to interpret great datasets by reducing the dimensionality of the whole dataset drastically while maintaining as much of the information from the original dataset as possible.\cite{25} The number of variables is finally reduced to two principal
components (PC) that most suitably describe the whole dataset. The different variables used for the PCA are arranged in the new coordinate system as arrows with arrows close together showing a high similarity.

PCA obtained from all 43 identified aroma active compounds visualize the relationship of the different components (Figure 2). The contribution of PC1 and PC2 to the whole information of the dataset was 66.4% and 9.4%, respectively, showing that the influence of PC1 was disproportionately high. Up to PC8 eigenvalues >1 were found indicating a significant influence of the PCs on the whole variance but >75% of the information can be mapped by PC1 and PC2. The loading matrix showed that most aroma active compounds contributed to PC1 with factors >0.9, while the contribution of the compounds to PC2 was much lower.

The loading plot of the orthogonal axes of the variables within the new coordinate system shows that most of the compounds are located in square I and IV close to PC1. This emphasis again that most of the aroma active compounds have high loading factors to PC1 since they run more or less parallel to this axis while the loading is more perpendicular to PC2. Considering the location of the argan oil samples in the coordinate system shows that different processing of the samples is mainly described by the occurrence of aroma active compounds on one side and the absence of aroma active compounds on the other side. Especially the quality of oil from roasted goat-digested almonds is characterized by a huge number of aroma active compounds because these oils are also found in square I and IV.

For identification of the aroma active compounds with highest influence on discrimination of the three classes of processed argan oils, two options are available. It is possible either to select compounds with the highest loading factors from the PCA or to carry out a one-way ANOVA to evaluate significant differences between the mean values of the three different types of argan oil. Due to the high number of compounds with high loading factors, the one-way ANOVA was conducted to compare the mean values of all aroma active compounds on basis of the peak areas between the three different types of argan oil processing on a significance level of $a = 0.05$. Only compounds showing significant differences between all three classes were used for the following improved differentiation by PCA.

In total, 17 compounds emphasized in Table 1 show significant differences for the three argan oil classes with the group of pyrazines (2,5-dimethylpyrazine, 2-ethyl-5-methylpyrazine, 2-ethyl-3,5-dimethylpyrazine, ethylpyrazine, 2,3-dimethylpyrazine, and 2,5-dimethylpyrazine) as most important compounds. Pyrazines are important products of the Maillard reaction but they are also formed as degradation products of different microorganisms such as Bacillus mutant,[26] Bacillus subtilis,[27] or Corynebacterium glutamicum.[28] Therefore, pyrazines may be detected in argan oil from roasted almonds as a result of the roasting process but also in higher amounts in argan oil from roasted, goat-digested almonds due to microbial degradation processes in the goat intestine. Additionally, four aldehydes (acetaldehyde, 3-methylbutanal, 2-methylpropanal, octanal), one alcohol (1-pentanol), and one ketone (2-hydroxypentan-3-one) as well as five unidentified compounds (TAGs) showed significant differences between the three classes of argan oil. Highest peak areas were found for almost all significant different compounds in argan oil from roasted, goat-digested almonds (87%) and the lowest for argan oil from unroasted almonds indicating the formation of degradation products from lipids and amino acids during fruit digestion in the goat. Only for 2-methylpropanal and 1-pentenol

![Figure 2. Biplot for PC1 and PC2 scores generated by PCA of 43 compounds identified as aroma active in argan oils from different processing (triangles, oil from unroasted almonds; rue, oil from roasted almonds; square, oil from roasted, goat-digested almonds).](image-url)
the highest amounts were found for argan oil from roasted almonds.

As typical markers for oxidation processes such as propanal, hexanal, 1-octen-3-one, or TAG 1844s97 m/z showed no significant differences between the classes, this result reveals that oxidation does not significantly contribute to the discrimination of the processed oils.

**Figure 3** shows the biplot as result of the PCA of the 17 aroma active compounds identified as significant different between the three different types of argan oil. The two components were able to map >90% (PC1 79.0%, PC2 11.7%) of the variance given by the 17 compounds. Looking on the eigenvalues, only PC1 (13.4) and PC2 (1.9) showed significant contributions of the PCs on the whole variance, whereas the eigenvalues of all the other components were below 1. Most of the loading factors of PC1 showed values >0.9, but only for 2-methylpropanal (0.49), 1-pentanol (0.63), 2-hydroxypropan-3-one (0.57), and TAG 1746.6s 67 m/z (0.71) the contribution for the separation of the different groups of argan oil was lower. The largest part for the differentiation of the samples was made by pyrazines with values between 0.95 and 0.99. 2-Methylpropanal (0.82), 1-pentanol (0.76), and 2-hydroxypropan-3-one (0.63) showed the highest contribution to PC2 while the loading factors of the other compounds were below ±0.3.

The biplot indicates the position of the different types of argan oil in a coordinate system. Observably samples arranged together according to the method of processing. Similarly to the PCA of all identified compounds, the separation of the three groups was mainly driven by PC1. Oils from unroasted almonds and oils from roasted, goat-digested almonds were located more or less on the same level of PC2 but on different levels of PC1 indicating that the separation of the groups was achieved by the high levels of the volatile compounds in oil from roasted, goat-digested almonds and the absence or low levels in oil from unroasted raw material. The oils obtained from roasted almonds are located between the oil from unroasted almonds and the oil from roasted, goat-digested almonds on PC1 but at a little higher level on PC2 due to the stronger influence of compounds such as 2-methylpropanol, 1-pentanol, or 2-hydroxypropan-3-one that are more influencing PC2.

### 3.5. Cluster Analysis

The 17 aroma active compounds identified in different reference oils as typical compounds with significant differences between the various types of processing were used to differentiate the quality of argan oils from the German market. In total, 13 different oils from the German market were included in the investigation, each measured twice resulting in 26 data points. According to the label, seven oils were obtained by extraction with a screw press from roasted almonds, two were extracted by hand malaxation and four were extracted by a screw press from un-roasted almonds. The sensory evaluation revealed that three oils obtained by screw-pressing from roasted and unroasted almonds were characterized by the attribute “cheese-like” indicating either the use of goat-digested fruits for the production of the oil or oil storage for a longer period of time.

Clustering of data is a statistical method used to classify complex data sets according to their characteristics enabling the identification of homogenous groups. Another advantage of this method is the visualization of the relationship between different samples. In comparison to PCA cluster analysis tries to find groups of samples that show a high similarity based on attribute values while the aim of PCA is to reduce a large number of
variables to a smaller number but losing as little information as possible.

In the present investigation, the different groups of samples from the German market were known, but clustering this data set on basis of the 17 characteristic compounds should show effectiveness of the selection of these compounds. Since clustering results in an unsupervised classification, a predefinition of classes was not necessary.

Figure 4 represents the cluster hierarchy of the samples displayed as tree diagram called a dendrogram. The clustering was achieved according to the Ward method. In this method for each cluster, the sum of the squared distances of the individual cases from the respective cluster centroid was calculated. After summing up these values, those two clusters were combined whose fusion results in the smallest increase of the total sum of the squared distances.

The figure illustrates the similarities of the samples on basis of the 17 volatile compounds that were also used in the PCA. The results are presented as measure of similarity. The higher the measure of similarity is, the lower is the similarity between the samples. A separation of the cluster branches at a high measure of similarity reflects a low sample similarity between groups belonging to different branches. In this study, the measure of similarity ranged from 0 to 12.4. First of all, the dendrogram shows a high similarity between the technical replicates of each sample by combining most of them together at a level <1. Second, it is striking that oils with a “cheese-like” impression and oils from unroasted almonds, respectively, clustered at the low similarity level of 3.8 (phenol line, dotted line in Figure 4). The high distance of both groups in the dendrogram also indicates the low similarity between them. Samples from roasted, mechanical extracted or roasted, manual extracted almonds were located between oils with “cheese-like” impression and from unroasted almonds. The grouping of these samples is not unambiguous at the distance measure of 3.8 indicating no high similarity between oils from manual and mechanical extracted almonds, respectively. If the measure of similarity is regarded at the higher level of round about four, five samples of manual (2) and mechanical (3) extracted oils clustered to oils with “cheese-like” impression, while two manual extracted oils clustered to the oils from unroasted almonds. A further view to the distance measure level of 6.2 indicates that most oils from roasted almonds, either manually or mechanically extracted showed a higher similarity to oils from roasted, goat-digested almonds as to oils from unroasted almonds. Considering results of statistical analysis presented in Table 1, these results were unexpected. The conducted statistical analysis revealed a lot of volatile compounds that are significant different between oil from roasted, goat-digested almond and oil from roasted or unroasted almonds, whereas between oil from roasted and unroasted almonds no significant difference was found. However, pyrazines show significant differences between all three groups, with lowest peak areas or no detection in oil from unroasted almonds. Due to these findings, it could be assumed that the presence of pyrazines dominates the result of the cluster analysis with higher similarity between oil from roasted and roasted, goat-digested almonds, respectively.

4. Conclusion
The present work has revealed some new information about the composition of aroma active volatile compounds extracted
by dynamic headspace from argan oils obtained by different processing. For the first time oils from goat-digested, roasted almonds have been included in the investigation of the aroma profile. These oils are characterized by a Roquefort cheese-like perception. Differences in the composition of volatile compounds between oils from unroasted and roasted argan almonds due to the occurrence of Maillard reaction products such as pyrazines could be shown. New is that these pyrazines also were found in oil from goat-digested and roasted almonds but in significant higher amounts. It can be assumed that these higher amounts of pyrazines resulted from microbial degradation when the kernels pass the intestine of the goats.

The present paper shows that the analysis of volatile aroma active compounds from argan oil in combination with statistical means such as PCA can be a strong analytical tool to classify various argan oil qualities. PCA revealed the contribution of individual volatile compounds obtained from dynamic headspace GC–MS analysis to the discrimination of the different samples. Using ANOVA, it is possible to identify compounds that show significant differences between the different groups of argan oil qualities allowing the best discrimination of the three groups. By this procedure, it is possible to reduce the number of aroma active compounds to the most important for the discrimination of different argan oil qualities. Finally, 17 compounds were used to differentiate argan oils successfully. In a cluster analysis, it was shown that these 17 volatile compounds successfully were applied to group argan oils from the German market according to their quality and processing.

The research on volatile compounds of argan oils is still at the beginning and the further validation of the method with a larger dataset is necessary, but the results of the present investigation showed that dynamic headspace analysis of the volatile compounds from argan oils in combination with GC–MS is a powerful tool to support the time- and labor-consuming sensory evaluation. In a next step, it would be necessary to measure and characterize more argan oils to increase the data pool for the further statistical evaluation. Then it would be possible to carry out linear discriminate analysis on the basis of the 17 compounds as significantly different identified compounds to calculate a discriminant function usable to discriminate the three groups of argan oil quality. For the practical application, this means that finally only 17 aroma active compounds have to be measured. The resulting area percentages for these compounds can be used to fill the variables of the resulting discriminant function to evaluate the quality of argan oil as oil from unroasted, roasted, or goat-digested, roasted almonds.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements
Parts of this research were supported by the German Ministry of Education and Research (FKZ 01DH12056). The authors are very thankful to the cooperatives La Cooperative Taitmatine, Taroudant, Morocco, and Tighanimine Filahia, Province Agadir, Morocco, for providing sample material.

Conflict of Interest
The authors declare no conflict of interest.

Keywords
argan oil, sensory evaluation, statistical approaches, volatile compounds

Received: July 8, 2019
Revised: September 30, 2019
Published online:

[1] Z. Charrouf, D. Guillaume, *Eur. J. Lipid Sci. Technol.* 2014, 116, 1316.
[2] Z. Charrouf, D. Guillaume, A. Driouch, *Biofutur* 2002, 220, 54.
[3] M. Hilali, Z. Charrouf, A. E. Aziz Soulhi, L. Hachimi, D. Guillaume, *J. Agric. Food Chem.* 2005, 53, 2081.
[4] B. Matthäus, L. Brühl, *Eur. J. Lipid Sci. Technol.* 2008, 110, 611.
[5] B. Matthäus, D. Guillaume, S. Gharby, A. Haddad, H. Harhar, Z. Charrouf, *Food Chem.* 2010, 120, 426.
[6] Z. Charrouf, H. El Hamchi, S. Mallia, G. Licitra, D. Guillaume, *Nat. Prod. Commun.* 2006, 1, 399.
[7] DGF, Deutsche Gesellschaft für Fettwissenschaft e. V. – Deutsche Einheitsmethoden zur Untersuchung von Fetten, Fettprodukten, Tensiden und verwandten Stoffen. Wissenschaftliche Verlagsgesellschaft, Stuttgart 2017.
[8] American Oil Chemists’ Society (AOCS), *Official Methods and Recommended Practices of the American Oil Chemist’s Society*, 7th ed., Urbana, IL, USA 2017.
[9] R. Aparicio-Ruiz, D. L. Garcia-Gonzalez, M. T. Morales, A. Lobrio-Prieto, I. Romero, *Talanta* 2018, 187, 133.
[10] T. H. Borges, E. Ramalhosa, I. Seiquer, J. A. Pereira, *Eur. J. Lipid Sci. Technol.* 2018, 120, 1700356.
[11] M. Fortini, M. Migliorini, C. Cherubini, L. Cecchi, L. Guerrini, P. Masella, A. Parenti, *Eur. J. Lipid Sci. Technol.* 2016, 118, 1213.
[12] G. Procida, A. Cichelli, C. Lagazio, L. S. Conte, *J. Sci. Food Agric.* 2016, 96, 311.
[13] A. Gracka, H. H. Jelen, M. Majcher, A. Siger, A. Kaczmarek, *J. Chromatogr. A* 2016, 1428, 292.
[14] A. Bonte, L. Brühl, K. Vosmann, B. Matthäus, *Eur. J. Lipid Sci. Technol.* 2017, 119, 1600259.
[15] H. El Monfalouti, Z. Charrouf, M. Giordano, D. Guillaume, B. Kartah, H. Harhar, S. Gharby, C. Denhez, G. Zeppa, *Nat. Prod. Comm.* 2013, 8, 33.
[16] M. Zaher, G. Reineccius, J.-P. Schirle-Keller, *Actes du Premier Congrès Intl. de l’Arganier, Agadir, Division de l’Information et de la Communication, Morocco 2011.*
[17] A. Gracka, M. Majcher, E. Kludskaja, J. Hradecky, J. Hajslova, H. H. Jelen, *J. Am. Oil Chem. Soc.* 2018, 95, 1475.
[18] B. Matthäus, L. Brühl, J. Verbraucherschutz Lebensmittelsicher. 2015, 10, 143.
[19] N. Kessler, H. Neuweger, A. Bonte, G. Langenkaemper, K. Niehaus, T. W. Nattkemper, A. Goesmann, *Bioinformatics* 2013, 29, 2452.
[20] G. Procida, B. Stancher, F. Cateni, M. Zacchigna, *J. Sci. Food Agric.* 2013, 93, 1035.
[21] R. Yaacoub, R. Saliba, B. Nsouli, G. Khalaf, I. Birlouez-Aragon, J. Agric. Food Chem. 2008, 56, 7082.
[22] C. Jacobsen, Eur. J. Lipid Sci. Technol. 1999, 101, 484.
[23] J. S. Elmore, M. A. Erbahadir, D. S. Mottram, J. Agric. Food Chem. 1997, 45, 2638.
[24] F. Ullrich, W. Grosch, Z. Lebensm.-Unters. Forsch. 1987, 184, 277.
[25] I. T. Jolliffe, J. Cadima, Philos. Trans. R. Soc. A 2016 374, 20150202.
[26] Z. J. Xiao, N. Z. Xie, P. H. Liu, D. L. Hua, P. Xu, Appl. Microbiol. Biotechnol. 2006, 73, 512.
[27] I. Besson, C. Creuly, J. B. Gros, C. Larroche, Appl. Microbiol. Biotechnol. 1997, 47, 489.
[28] J. S. Dickschat, S. Wickel, C. J. Bolten, T. Nawrath, S. Schulz, C. Wittmann, Eur. J. Org. Chem. 2010, 2010, 2687.
[29] S. Poehlmann, P. Schieberle, J. Agric. Food Chem. 2013, 61, 2933.
[30] T. Matsui, H. Guth, W. Grosch, Fett/Lipid 1998, 100, 51.