



In-depth profiling of the key odor-active compounds in commercially dried red and black goji berries

Yan Zheng¹ · Claudia Oellig¹ · Lin Zhu² · Michael Granvogl¹ · Yuan Liu^{3,4} · Yanping Chen⁴ · Xiaoxiao Feng⁴ · Wenli Wang⁴ · Yanyan Zhang²

Received: 7 March 2025 / Revised: 12 March 2025 / Accepted: 13 April 2025 / Published online: 7 May 2025
© The Author(s) 2025

Abstract

To get information on the aroma profiles of both commercial dried red goji berries (*Lycium barbarum* L.) and black goji berries (*Lycium ruthenicum* M.), key odor-active compounds in both commercial berries were elucidated. Sensory evaluation revealed similar but weaker aroma profiles in black goji berries. By applying solvent-assisted flavor evaporation, aroma fractionation, aroma extract dilution analysis, and gas chromatography analysis, 45 and 39 odor-active compounds were detected in red and black goji berries, respectively, compared to the authentic references. Acetic acid was the predominant odor-active compound in both berries. Most of the key odor-active compounds were the same in both berries, but their contents were significantly different ($p < 0.05$). Among these odor-active compounds, 11 compounds were first reported in goji berries. After aroma reconstitution, (*E*)- β -damascenone, (*E*)-2-nonenal, and (*E,E*)-2,4-nonadienal, etc. are verified as the key odor-active compounds in red goji berries and responsible for cooked apple-like, green, and fatty, etc. odors. While dried black goji berries displayed a distinct stronger fruity aroma. Most of the key odor-active compounds in both berries were lipid derivatives generated from carotenoids and fatty acids. The results can be applied to the food quality control of commercial goji products.

Keywords Red goji berry · Black goji berry · Solvent-assisted flavor evaporation · Key aroma · Fractionation · Aroma recombination

The author Prof. Dr. Micheal Granvogl has passed away.

✉ Yanyan Zhang
yanyan.zhang@uni-hohenheim.de
Yan Zheng
yan.zheng@uni-hohenheim.de
Claudia Oellig
claudia.oellig@uni-hohenheim.de
Lin Zhu
lin.zhu@uni-hohenheim.de
Yuan Liu
y_liu@sjtu.edu.cn
Yanping Chen
catherinechenyp@sjtu.edu.cn
Xiaoxiao Feng
fxxhzl@sjtu.edu.cn

Wenli Wang
wenli-wang@sjtu.edu.cn

- ¹ Department of Food Chemistry and Analytical Chemistry (170a), University of Hohenheim, Garbenstraße 28, 70599 Stuttgart, Germany
- ² Department of Flavor Chemistry (150h), University of Hohenheim, Fruwirthstraße 12, 70599 Stuttgart, Germany
- ³ School of Food Science and Engineering, Ningxia University, Yinchuan 750021, P.R. China
- ⁴ School of Agriculture and Biology, Department of Food Science and Technology, Shanghai Jiao Tong University, Dongchuan Road 800, Shanghai 200240, P.R. China

Introduction

Goji berry is the fruit of *Lycium* species (*Solanaceae* family) [1]. Among ~100 different species of *Lycium*, red goji berries (especially *Lycium barbarum* L.) and black goji berries (*Lycium ruthenicum* M.) are regarded as the most typical types of goji berries [1, 2]. In numerous traditional medicinal monographs, the pharmacological properties of goji berries were well-documented, such as nourishing the liver and kidneys and benefiting eyesight [1, 3]. Modern research reported the various biological functions of goji berries and demonstrated similarities and differences in the nutritional components between red and black goji berries, including carotenoids [4, 5], fatty acids [2], anthocyanins [6], and polyphenols [5].

Food flavor is a key criterion for food quality and relates to the food market and customer consumption. So far, only a few studies researched the flavor compositions of goji berries. In dried red goji berries, Kim *et al.* detected 130 volatiles, including acids, alcohols, aldehydes, alkanes, etc [7]. Targeting the trace amounts and high-volatile compounds, Chen *et al.* applied a combination of low-temperature enrichment and headspace extraction to determine 57 volatiles in dried red goji berries [8]. According to the principle of encoding the key odor-active codes, only a small subset of volatile components elicited the smell of a given food [9]. The odor-active compounds must be perceivable using odorant receptors in the human olfactory system [9]. Thus, Lu *et al.* applied aroma extract dilution analysis (AEDA) using gas chromatography with olfactometry (GC/O) and found only 15 volatiles with high flavor dilution (FD) factors in red goji berries [10]. Similarly, among the 33 odor-active compounds sniffed at by GC/O, (*E*)-2-heptenal, hexanal, 1-octen-3-ol, acetic acid, and 3-hydroxy-2-butanone were found as the most contributing odor-active compounds and donated mushroom-like, pungent, vinegar-like, green, and grassy odor impressions to dried red goji berries [11]. However, most research has focused on the volatiles of goji berries, with identification relying solely on mass spectra rather than comparisons with authentic reference data, potentially compromising the accuracy of the results.

Although volatile compounds were abundant in types and amounts in goji berries, among the reported numerous volatiles in goji berry products, only <80 volatiles were assigned as odor-active compounds in red goji berries [10]. For example, with the assistance of the human sensory system, a sensory-guided investigation suggested that 17 of 83 volatile compounds had odor activity values (OAV) > 1 in red goji berry pulp [12]. Moreover, such comprehensive data on odor-active compounds was limited to red goji berries. Although a recent investigation indicated that red and black goji berries were characteristic in the volatiles' types and

quantities and easily distinguished based on these volatiles [13], very few investigations have reported the odor-active compounds in black goji berries. At this point, the odor-active compounds and the flavor comparison between red and black goji berries were also not clear. Due to the commercially dried goji berries were reported to be pretreated with the physical or chemical approach and processed with different drying processes all over the world [14], it is meaningful to focus on the odor-active compounds in the commercially dried goji berries. As the clarification of the sensomics approach [15], odor-active compounds could not be assigned as key odor-active compounds unless the naturally occurring concentrations surpassed their odor thresholds (OTs) in the food matrix and sensorial evaluated by aroma reconstitution. Due to the lack of sensory evaluation, the unique odor properties and the key odor-active compounds of dried red and black goji berries are still unclear.

Therefore, we aimed at (i) the screening and comparison of the odor-active compounds in dried red and black goji berries by comparative aroma extract dilution analysis (cAEDA) using GC/O; (ii) determination of odor-active compounds' contents using (isotopically labeled) internal standards; afterward, key odor-active components were (iii) assigned from the calculation of the OAVs (the ratios of the concentrations to their respective OTs); and further (iv) validated by the aroma recombination tests and aroma profile analysis (APA). These data are further used to characterize the total set of key odor-active compounds in two types of goji berries. Additionally, 2-acetyl-1-pyrroline, 2-propionyl-1-pyrroline, and *trans*-4,5-epoxy-(*E*)-2-decenal were synthesized in our study because these references were not commercially available. A detailed analysis of the differences and relationships between the key odor-active compounds in commercial dried red and black goji berries can guide consumers in selecting products and support food control and supervision efforts, particularly from the perspective of the overall aroma profile.

Materials and methods

Chemicals

The references and chemicals were commercially purchased: 2-chloro-4,6-dimethoxy-1,3,5-triazine (CDMT; 98%), diethyl ether (DEE; ≥ 99.5%), phenol (≥ 99%), 3-phenylpropanoic acid (99%), γ -undecalactone (98%), vanillin (99%) (Acros Organics; Thermo Fisher Scientific, Nidderau, Germany); 2-acetylpyridine (98%), butanoic acid (99%), decanoic acid (99%), dodecanal (95%), ethyl 3-methylbutanoate (98%), hexanal (98%), 2-methylbutanoic acid (98%), 4-methylmorpholine (99%), δ -nonalactone (98%),

pentanoic acid (99%), phenylacetic acid (99%), tetrahydrofuran (THF; $\geq 99.8\%$) (Alfa Aesar, Karlsruhe, Germany); 3-isobutyl-2-methoxypyrazine (99.6%), (*E,Z*)-2,6-nonadienal (96% mixture isomers), 1-octen-3-one (97.7%) (BLD pharm, Karlsruhe, Germany); dichloromethane (DCM; for HPLC), sodium hydrogen carbonate (NaHCO_3 ; $\geq 99\%$), sodium hydroxide (NaOH ; $\geq 99\%$), 2-phenylethanol (99%) (Carl Roth, Karlsruhe, Germany); acetic acid ($\geq 99\%$), maltol (98%) (Fluka, Neu-Ulm, Germany); *N,O*-dimethyl hydroxylamine (for synthesis) (Fluorochem, Hadfield, UK); sodium sulphate (Na_2SO_4 ; specification as European Pharmacopoeia (Reag. Ph. Eur.)) (Häberle Labortechnik, Lonsee, Germany); *L*-proline (Ph. Eur.) (ITW Reagents, Darmstadt, Germany); 3-hydroxy-4,5-dimethyl-2(*5H*)-furanone (97.5%), (*E*)- β -ionone (96%), linalool (98%), 2-methoxy-4-vinylphenol (98%), 3-methylbutanoic acid (99%), (*E,E*)-2,4-nonadienal (85%) (J&K scientific Ltd, Shanghai, China); silica gel 60 (0.04–0.063 mm) (Macherey-Nagel, Düren, Germany); decanal (97%), eugenol (Ph.Eur.), hydrochloric acid (HCl ; 37%) (Merck, Darmstadt, Germany); di-*tert*-butyl dicarbonate ($\geq 98\%$), 3-chloroperbenzoic acid ($\leq 77\%$), (*E*)- β -damascenone (1.1–1.4%), ethylmagnesium bromide (3.0 M in DEE), 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone (99%), methylmagnesium bromide (3.0 M in DEE), γ -nonalactone (97%), octanal (99%), octanoic acid ($\geq 98\%$), 2-phenylethyl acetate (99%), trifluoroacetic acid (99%) (Sigma-Aldrich Chemie, Taufkirchen, Germany); *m*-cresol ($>98\%$), hexanoic acid ($>98\%$), 3-methyl-2,4-nonanedione ($>97\%$), nonanal (95%), (*E*)-2-nonenal ($>95\%$) (TCI, Eschborn, Germany); ethanol (for HPLC) (Th.Geyer, Renningen, Germany); *n*-pentane ($\geq 99.7\%$, VWR, Darmstadt, Germany); argon (99.996%), hydrogen (99.999%), liquid nitrogen, nitrogen (99.95%) (Westfalen, Münster, Germany).

The stable isotopically labeled references, [$^2\text{H}_3$]-vanillin, [$^2\text{H}_2$]-butanoic acid, [$^{13}\text{C}_2$]-phenylacetic acid, and [$^2\text{H}_2$]-3-methylbutanoic acid, were obtained from Prof. Dr. Michael Granvogl. DEE was freshly distilled and stabilized by adding potassium hydroxide (VWR, Darmstadt, Germany).

Syntheses

Several odor-active compounds were not commercially available. However, the precise identification should be compared to the data with the authentic references. Therefore, these odor-active compounds were synthesized as mentioned below.

2-Acetyl-1-pyrroline (V in Fig. 1a) and 2-propionyl-1-pyrroline (VII in Fig. 1a)

As shown in Fig. 1a, V was synthesized in a four-step route starting from *L*-proline (I in Fig. 1a) as in previous procedures [16] with minor modifications.

N-(*tert*-butoxycarbonyl)-*L*-proline (II in Fig. 1a).

I (4 mmol) in 10 mL of DCM was supplemented with 12.5 mmol of 4-methylmorpholine and 6 mmol of di-*tert*-butyl dicarbonate. The suspension was turned clear after magnificently stirring for 2 h at room temperature to obtain II, followed by the supplementation of 10 mL of THF. The solvent was exchanged for THF after concentration under reduced pressure and adjusted to 20 mL with THF.

N-(*tert*-butoxycarbonyl)-*L*-proline-*N'*-methoxy-*N'*-methylamide (III in Fig. 1a).

The suspension with 6 mmol of 2-chloro-4,6-dimethoxy-1,3,5-triazine and II was reacted for 2 h on magnetic stir at room temperature, followed by stirring with *N,O*-dimethyl hydroxylamine (6.3 mmol) for a whole night at room temperature. After filtering and washing with THF, the mixture was then concentrated in a rotary evaporator before the next step.

2-Acetyl-*N*-(*t*-butoxycarbonyl)-pyrrolidineert (IV in Fig. 1a)

The THF solution containing III was drop-by-drop supplemented with the excess amounts of methylmagnesium bromide (12.5 mmol) and reacted at room temperature on a magnific stir for 5 h under an argon atmosphere. After cooling in crushed ice, the reaction was stopped by adding HCl (5 mol/L) until pH 3. The suspension was then neutralized with aqueous NaOH (5 mol/L), followed by separation with DEE (3×100 mL) and a saturated NaHCO_3 solution (3×50 mL). After drying, the combined upper phase was evaporated to dryness to yield IV in rotary evaporation.

2-Acetyl-1-pyrroline (V in Fig. 1a)

IV in 10 mL of DCM was supplemented with trifluoroacetic acid (3 mL) and stirred in an ice bath for 1 h. The suspension was supplemented with 20 mL of DEE and aqueous NaOH (5 mol/L) to adjust the pH to 7, then separated with DEE (3×30 mL). The upper phase was combined, dried, concentrated, followed by fractionated with stepwise elution as follows by water-cooled flash chromatography (30 cm $\times$ 1 cm, 10–12 °C water circulation) packed with activated silica gel (15 g): 50 mL *n*-pentane, 50 mL 90:10 *n*-pentane: DEE (v:v), 50 mL 80:20 *n*-pentane: DEE (v:v), 50 mL 70:30 *n*-pentane: DEE (v:v), 50 mL 60:40 *n*-pentane: DEE (v:v), 50 mL 50:50 *n*-pentane: DEE (v:v), 50 mL 40:60 *n*-pentane: DEE (v:v), and 50 mL DEE. The MS spectrum of V was displayed in Fig. S1a. and ions (*m/z* values) with intensity $\geq 5\%$ were listed as follows:

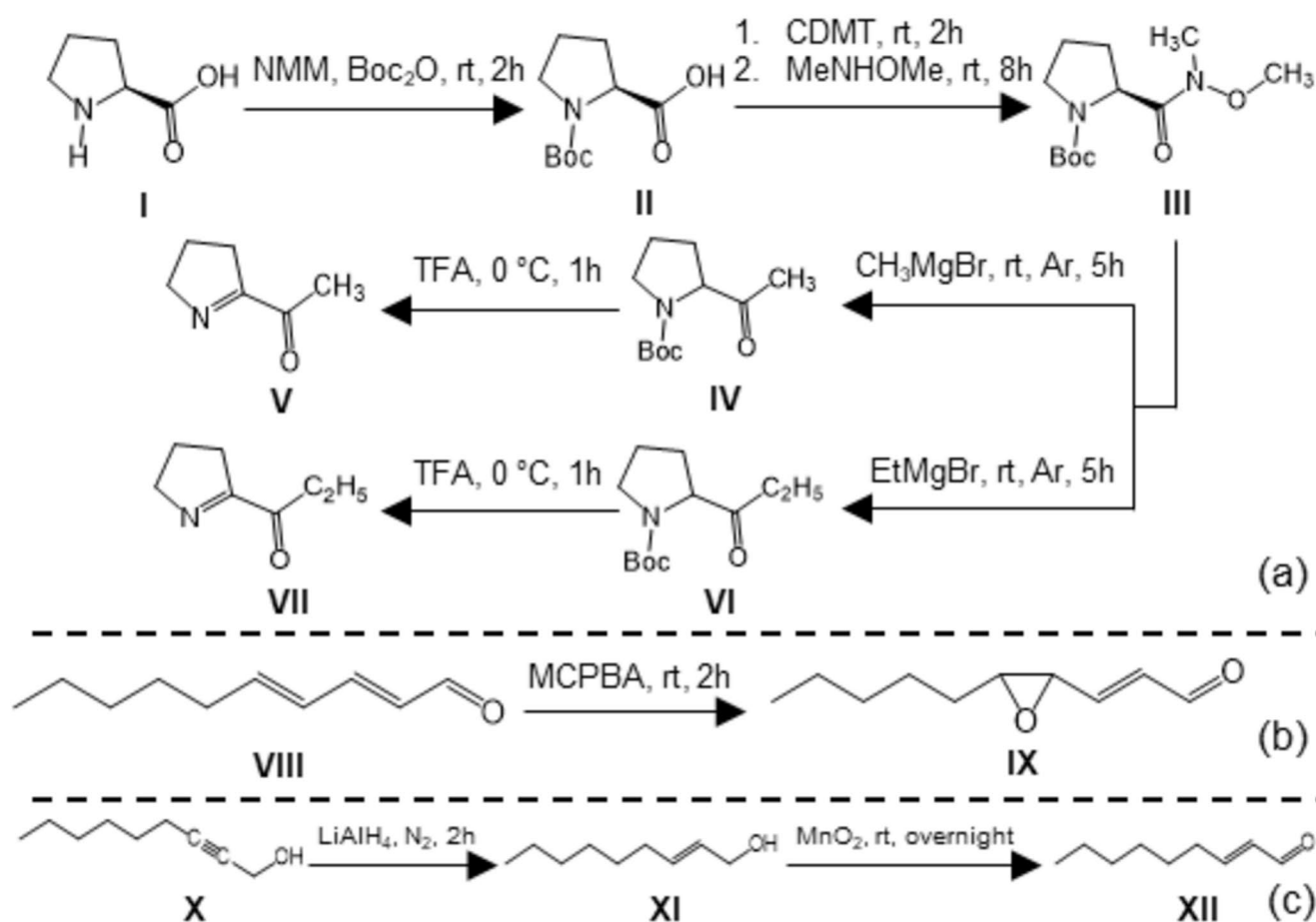


Fig. 1 Synthesis routes of (a) 2-acetyl-1-pyrroline (V) and 2-propionyl-1-pyrroline (VII), and (b) *trans*-4,5-epoxy-(*E*)-2-decenal (IX). NMM 4-methylmorpholine; Boc_2O di-*tert*-butyl dicarbonate; *rt* room temperature; CDMT 2-chloro-4,6-dimethoxy-1,3,5-triazine; MeNHOMe, *N,O*-

dimethyl hydroxylamine; CH_3MgBr methylmagnesium bromide; *Ar* argon atmosphere; TFA trifluoroacetic acid; EtMgBr ethylmagnesium bromide; MCPBA 3-chloroperbenzoic acid

GC/MS (EI, 70 eV): *m/z* (rel int., %): 43 (100), 83 (61), 41 (55), 42 (27), 68 (23), 111 (19), 69 (18), 39 (13), 82 (7), 40 (7).

2-Propionyl-1-pyrroline (VII in Fig. 1a)

VII was formed using ethylmagnesium bromide instead of methylmagnesium bromide and purified as mentioned for the synthesis of V (Fig. S1b).

GC/MS (EI, 70 eV): *m/z* (rel int., %): 97 (100), 57 (97), 41 (68), 69 (66), 96 (36), 68 (18), 88 (9).

trans-4,5-Epoxy-(*E*)-2-decenal (IX in Fig. 1b)

IX was developed by epoxidation of (*E, E*)-2,4-decadienal (VIII) using 3-chloroperbenzoic acid as previously described [17] (Fig. 1b). VIII (3 mmol) in DCM (10 mL) was dropwisely supplemented with 3-chloroperbenzoic acid (3 mmol) in DCM (30 mL). The suspension was allowed to stand for 1 h and stored in the freezer overnight. After twice extracted with NaHCO_3 solution (0.5 mol/L, 50 mL each time) and dried over Na_2SO_4 , the organic phase was distilled

to ~1 mL. The concentrate was loaded onto a water-cooled column chromatography equipped with 15 g silica gel and conditioned by 100 mL *n*-pentane:DEE (95:5, *v:v*) solution. Then, the concentrate was stepwise purified with the *n*-pentane/DEE mixtures (*v:v*): 120 mL (90:10, fraction 1), 50 mL (80:20, fraction 2), and 120 mL (70:30, fraction 3). The solvent of fraction 3 was distilled off to yield IX (Fig. S1c), and *cis*-isomer was the side product (35%) (Fig. S1d).

GC/MS (EI, 70 eV): *m/z* (rel int., %): 68 (100), 81 (25), 39 (15), 41 (13), 43 (13), 55 (11), 69 (10), 57(6), 67 (6).

Materials

Respective ten kilograms of commercially dried red goji berries (red or dark red hue, *Lycium barbarum* L.) and black goji berries (purple-black hue, *Lycium ruthenicum* M.) were originally harvested from China, online purchased from the same manufacturer (Zhongning, Ningxia, China) in 2019, and stored in dark at room temperature. The drying process of both berries was claimed to be sun-dried at the early stage

and subjected to hot-air drying to get final commercial-dried products. Due to the residual moisture and high sugar contents, the berries were ground with double the amount of anhydrous Na_2SO_4 in a Freezer/Mill (Spex CertiPrep 6800, U.S.A) with liquid nitrogen to avoid artificial aroma variation and get a fine powder. The powder samples were stored at -20°C before the next steps.

Isolation of the volatiles

The sample powder (60 g, a mixture of 20 g dried goji berries and 40 g Na_2SO_4) was extracted overnight with DCM (240 mL) at room temperature on magnetic stir. After filtering, the residue was washed twice with DCM (60 mL each time) for 1 h. The organic extracts were combined and subsequently distilled using the SAFE technique [18] with a constant temperature of 40°C to eliminate the non-volatiles. After drying over anhydrous Na_2SO_4 , the distillate was concentrated to $\sim 200\ \mu\text{L}$ using a Vigreux column ($50 \times 1\ \text{cm}$) and a microdistillation apparatus at 53°C .

Column chromatography

To prevent superimposition by more abundant volatile compounds, the SAFE distillate in DCM ($\sim 50\ \text{mL}$) was separated into biphasic with aqueous NaHCO_3 solution ($0.5\ \text{mol/L}$, $3 \times 50\ \text{mL}$) [19]. The combined organic phase was concentrated to $\sim 1\ \text{mL}$ (neutral/basic fraction, NBF), and further separated on a water-cooled column as mentioned in Section “2-Acetyl-1-pyrroline (V in Fig. 1a) and 2-propionyl-1-pyrroline (VII in Fig. 1a)” depending on the volatile polarity. After the test of pre-experiments, the following gradients were used: $50\ \text{mL}$ *n*-pentane (NBF1), $50\ \text{mL}$ 90:10 *n*-pentane: DEE (v:v) (NBF2), $50\ \text{mL}$ 80:20 *n*-pentane: DEE (v:v) (NBF3), $50\ \text{mL}$ 50:50 *n*-pentane: DEE (v:v) (NBF4), and $50\ \text{mL}$ DEE (NBF5). Each portion was dried and concentrated to $\sim 200\ \mu\text{L}$. The combined aqueous phase was supplemented with HCl solution ($5\ \text{mol/L}$) until pH 2, then extracted three times with DEE ($100\ \text{mL}$ each). The organic phases were combined, dried, and concentrated to $\sim 200\ \mu\text{L}$ (acidic fraction, AF).

Gas chromatograph with olfactometry (GC/O)

For the GC/O analysis, the deactivated capillary column ($5\ \text{m} \times 0.32\ \text{mm}$ i.d.) was performed as the pre-column and a polar or nonpolar capillary column (DB-FFAP or DB-5; both $30\ \text{m} \times 0.32\ \text{mm}$ i.d., $0.25\ \mu\text{m}$ film thickness; J&W Scientific, Agilent Technologies, Waldbronn, Germany) was used as the main column as previously description [20]. The sample ($2\ \mu\text{L}$) was subjected to a cool-on-column inlet in a gas chromatograph (type 5160, Carlo Erba Instruments,

Milano, Italy), which was kept at 40°C for 2 min, then heated to 230°C at $6^\circ\text{C}/\text{min}$, and stayed at 230°C for 5 min. The gas flow was equally split to the flame ionization detector (FID) and the sniffing port. The constant flow rate was set as $1.6\ \text{mL}/\text{min}$. Both detector temperatures were set at 230°C . Each component was calculated as its retention index (RI) with a mixture of $\text{C}_6\text{--C}_{26}$ or $\text{C}_6\text{--C}_{19}$ *n*-alkanes for DB-FFAP or DB-5 column.

Comparative aroma extract dilution analysis (cAEDA)

The concentrated SAFE distillate was 1:1 (v:v) stepwise diluted with DCM and analyzed by GC/O to get the FD factors for the screening of the important odor-active compounds [21]. FD factor of each odor-active compound was the highest dilution factor of the original SAFE distillate when the smell can be perceived on GC/O. Each sample was prepared and measured in triplicate, and the result was averaged.

Gas chromatography with mass spectrometry (GC/MS)

According to the method mentioned previously [20], a Thermo Fisher Trace GC type 1300 system (Dreieich, Germany) was equipped with a splitless inlet and a fused silica capillary column (either DB-5 or DB-FFAP, both $30\ \text{m} \times 0.25\ \text{mm}$ i.d., $0.25\ \mu\text{m}$ film thickness; J&W Scientific, Agilent Technologies, Waldbronn, Germany) and connected with a Thermo ISO 7000 single quadrupole mass spectrometer (Dreieich, Germany). Injection volume, oven temperature, and flow rate were set as mentioned in Section “Gas chromatograph with olfactometry (GC/O)”. The mass spectra of compounds were generated in full scan (m/z 35–300) and electron ionization (EI) mode at $70\ \text{eV}$. The MS transfer line and ion source temperatures were set at 250°C . Blank runs were performed after three to ten samples to rule out sample carryover and ensure analytical accuracy.

Two dimensional-gas chromatography with mass spectrometry (2D-GC/MS)

The sample ($1\ \mu\text{L}$) was injected through an on-column inlet (purge flow of $5\ \text{mL}/\text{min}$) into the first Thermo Scientific trace 1300 GC (Dreieich, Germany) that was equipped with DB-FFAP fused silica capillary column and an FID (250°C) by a Thermo TriPlus RSH autosampler (Dreieich, Germany) [20]. The carrier gas (helium) was set at a consistent flow rate of $3.7\ \text{mL}/\text{min}$. About 1 min of the effluent was cut, flowed into the second Thermo Scientific trace 1310 GC (Dreieich, Germany) equipped with a DB-5

capillary column via a back trap which remained at 250 °C, and then analyzed from 1.5 min by the MS. The MS parameters were as mentioned in Section “[Gas chromatography with mass spectrometry \(GC/MS\)](#)”. The rest of the effluent was detected and analyzed by the FID on the first GC. A constant flow (helium) of 11.5 mL/min was set for the dean switch. Both oven temperature programs of the two GCs were set the same as mentioned in Section “[Gas chromatography with olfactometry \(GC/O\)](#)”.

Quantitation of odor-active compounds in dried red and black goji berries

The internal standards used for the quantitation were selected as 2-methylvaleric acid (IS1, targeting the acids and aldehydes), thymol (IS2, targeting the phenols and alcohols), α -methyl- γ -butyrolactone (IS3, targeting esters and ketones), [$^2\text{H}_3$]-vanillin (targeting vanillin), [$^2\text{H}_2$]-butanoic acid (targeting butanoic acid), [$^{13}\text{C}_2$]-phenylacetic acid (targeting phenylacetic acid), and [$^2\text{H}_2$]-3-methylbutanoic acid (targeting 2- and 3-methylbutanoic acid). The IS and analytes (2–50 $\mu\text{g/mL}$) were prepared in DCM at concentration ratios of 1:5, 1:3, 1:1, 3:1, and 5:1. The peak areas (range of 10^5 to 10^8 count*min) were obtained from GC/MS in selected ions-monitoring (SIM) mode. The concentration ratios (x -axis) and the respective peak areas (y -axis) were used for the calibration curves (Table 1). Considering the data estimated from preliminary experiments, the internal standards (each 2–50 μg) were equilibrated with goji berry powder (30–150 g) for 30 min and then isolated the volatiles from nonvolatiles as mentioned in Section “[Isolation of the volatiles](#)”.

Sensory analyses

The sensory analysis of goji berries was performed with the approval of the Ethics Committee of the University of Hohenheim. A sensory panel of eight experienced aroma evaluators (25–31 years old) was involved in sensory analyses at room temperature. The participants were aware of the relevant risks and the purpose of the evaluation. They are voluntarily participating. Moreover, all the used odor-active compounds were approved by the European Union (EU) and the European Food Safety Authority (EFSA).

Aroma profile analysis (APA)

The odor attributes were selected as cooked apple-like ((*E*)- β -damascenone), mushroom-like (1-octen-3-one), hay-like (3-methyl-2,4-nonanedione), fatty ((*E*)-2-nonenal), fruity (ethyl 3-methylbutanoate), and floral ((*E*)- β -ionone). The odor references were dissolved in ethanol and then diluted

at a concentration of 100-fold of their OTs in water. For sensory analyses, dried goji berry samples (5 g) were weighed into a Teflon vessel. The panelists rated each odor intensity in goji berry samples from 0 (no intensity) to 3 (strong intensity) with an increment of 0.5.

Aroma reconstitution

The respective odorless matrix was prepared according to the previous investigation with minor modifications [19]. The raw materials (~60 g dried red goji berries) were extracted with three times the amounts of DCM (~180 mL) for one week on the magnetic stir. The solvents were separated, and the residues were extracted twice, as described in Section “[Isolation of the volatiles](#)”. Afterward, the thoroughly washed residues were blown off the rest of the odor-active compounds for over a month and used as the odorless matrix. Based on the determined contents of the original goji berry samples, all the odor-active components with OAVs (the ratio of the determined concentration to the respective OT) ≥ 1 were mixed in the respective odorless matrix. The aroma evaluation of the recombinant (5 g) was executed using the same procedure as mentioned in Section “[Aroma profile analysis \(APA\)](#)”. at room temperature.

Statistical analysis

APA data and contents of commercially dried red goji berries and commercially dried black goji berries were estimated for the differences by *t*-test (Excel function TDIST, Excel 2016). Significant differences were based on $p < 0.05$.

Results and discussion

Overall aroma profiles of the original dried red and black goji berries

The APA was executed to get the first impression of the overall aroma profiles of commercially dried red and black goji berries (Fig. 2). Both goji berries evoked comparable odor descriptions and odor intensities, especially in cooked apple-like, hay-like, and fruity. No odor intensity of both berries had a significant difference ($p > 0.05$, data not shown). Fruity was the strongest odor description, and mushroom-like was weakest in both goji berries. The main variation between the aroma properties of the two goji berries was the stronger fatty smell detected in commercially dried red goji berries. In contrast, commercially dried black goji berries displayed more intensive odor notes of mushroom-like and floral flavor.

Table 1 The internal standards, quantifier ions, and calibration curves of the odor-active compounds in commercially dried red and black goji berries

Analyte substance	Internal standard ^a		Quantifier ion (m/z) ^b		Calibration curve ^c	R ²
	an.	in.				
Butanoic acid	[² H ₂]-Butanoic acid	73	74		y = 0.9195x + 0.0304	0.9959
2-Methylbutanoic acid ^d	[² H ₂]-3-Methylbutanoic acid	60	63		y = 0.7209x + 0.0035	0.9992
3-Methylbutanoic acid ^d	[² H ₂]-3-Methylbutanoic acid	60	63		y = 0.7209x + 0.0035	0.9992
Phenylacetic acid	[¹³ C ₂]-Phenylacetic acid	91	92		y = 1.1881x + 0.6746	0.9990
Vanillin	[² H ₃]-Vanillin	151	154		y = 1.1562x - 0.0632	0.9991
Hexanal	IS1	56	74		y = 0.5303x - 0.157	0.9992
Octanal	IS1	84	74		y = 0.9953x - 0.033	0.9999
Nonanal	IS1	57	74		y = 0.4592x - 0.1232	0.9991
(E)-2-Nonenal	IS1	55	74		y = 1.5951x - 0.3383	0.9994
Decanal	IS1	57	74		y = 0.2255x - 0.1106	0.9909
(E, E)-2,4-Nonadienal	IS1	81	74		y = 1.2215x - 0.4857	0.9904
trans-4,5-Epoxy-(E)-2-decenal	IS1	68	74		y = 0.7942x - 0.1922	0.9998
Acetic acid	IS1	60	74		y = 0.0979x - 0.0285	0.9915
Pentanoic acid	IS1	60	74		y = 0.6442x - 0.1253	0.9914
Hexanoic acid	IS1	60	74		y = 0.6726x - 0.0856	0.9974
Octanoic acid	IS1	60	74		y = 0.5738x + 0.0405	0.9921
Decanoic acid	IS1	73	74		y = 0.3651x + 0.0143	0.9967
3-Phenylpropanoic acid	IS1	91	74		y = 0.7505x - 0.1178	0.9902
Ethyl 3-methylbutanoate	IS2	88	56		y = 1.9993x - 0.6675	0.9963
1-Octen-3-one	IS2	55	56		y = 1.8307x - 0.8481	0.9908
4-Hydroxy-2,5-dimethyl-3(2H)-furanone	IS2	128	56		y = 0.8397x - 0.0098	0.9945
3-Hydroxy-4,5-dimethyl-2(5H)-furanone	IS2	83	56		y = 0.4511x - 0.0787	0.9925
2-Acetylpyridine	IS2	79	56		y = 1.3849x - 0.601	0.9919
3-Methyl-2,4-nonanedione	IS2	99	56		y = 2.0085x - 0.2423	0.9935
(E)-β-Damascenone	IS2	69	56		y = 0.0343x - 0.0027	0.9988
γ-Nonalactone	IS2	85	56		y = 3.8439x - 0.5049	0.9905
Maltol	IS2	126	56		y = 1.3077x - 0.4501	0.9912
(E)-β-Ionone	IS2	177	56		y = 3.1642x - 0.0314	1
γ-Undecalactone	IS2	85	56		y = 2.6011x - 0.6311	0.9957
2-Phenylethyl acetate	IS2	104	56		y = 5.4947x - 0.3809	0.9957
Linalool	IS3	71	135		y = 0.309x + 0.0407	0.9928
2-Phenylethanol	IS3	91	135		y = 0.8254x - 0.0142	0.9992
Phenol	IS3	94	135		y = 0.6208x - 0.1668	0.9926
m-Cresol	IS3	107	135		y = 0.3843x + 0.033	0.9930
Eugenol	IS3	164	135		y = 0.2948x + 0.0933	0.9906
2-Methoxy-4-vinylphenol	IS3	135	135		y = 0.4321x - 0.0021	0.9998

^aIS1, 2-methylvaleric acid; IS2; α-methyl-γ-butyrolactone; IS3, thymol^bThe quantitation/semi-quantitation was carried out by extracting the specific ions in EI mode; an., analyte; in., internal standard^cThe calibration curve was established with the concentration ratio of the analyte and internal standard as the x-axis and the peak area ratio of the analyte and internal standard as y-axis^dAnalytes determined the sum of 2- and 3-methyl isomers and 3-methylbutanoic acid and its labeled reference was used for calibration

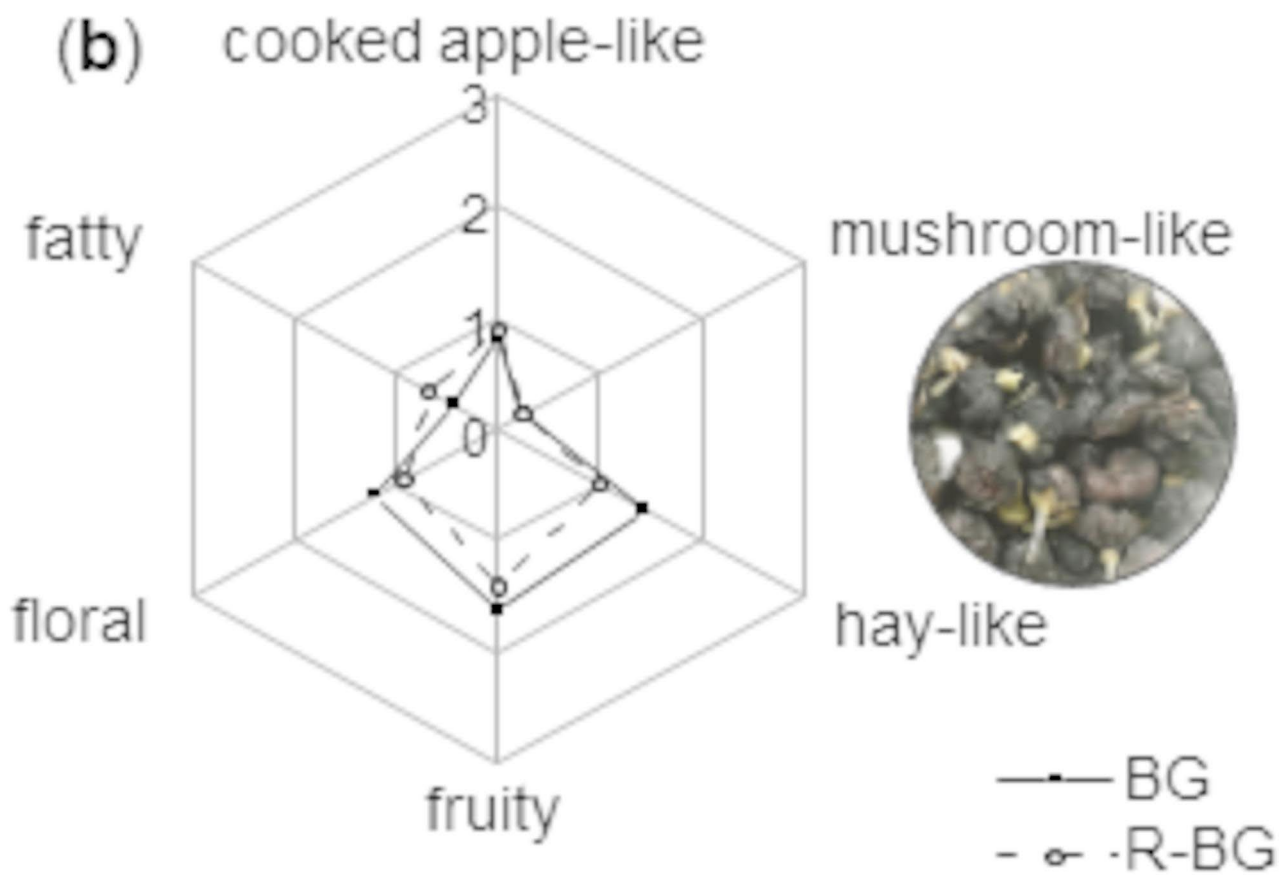
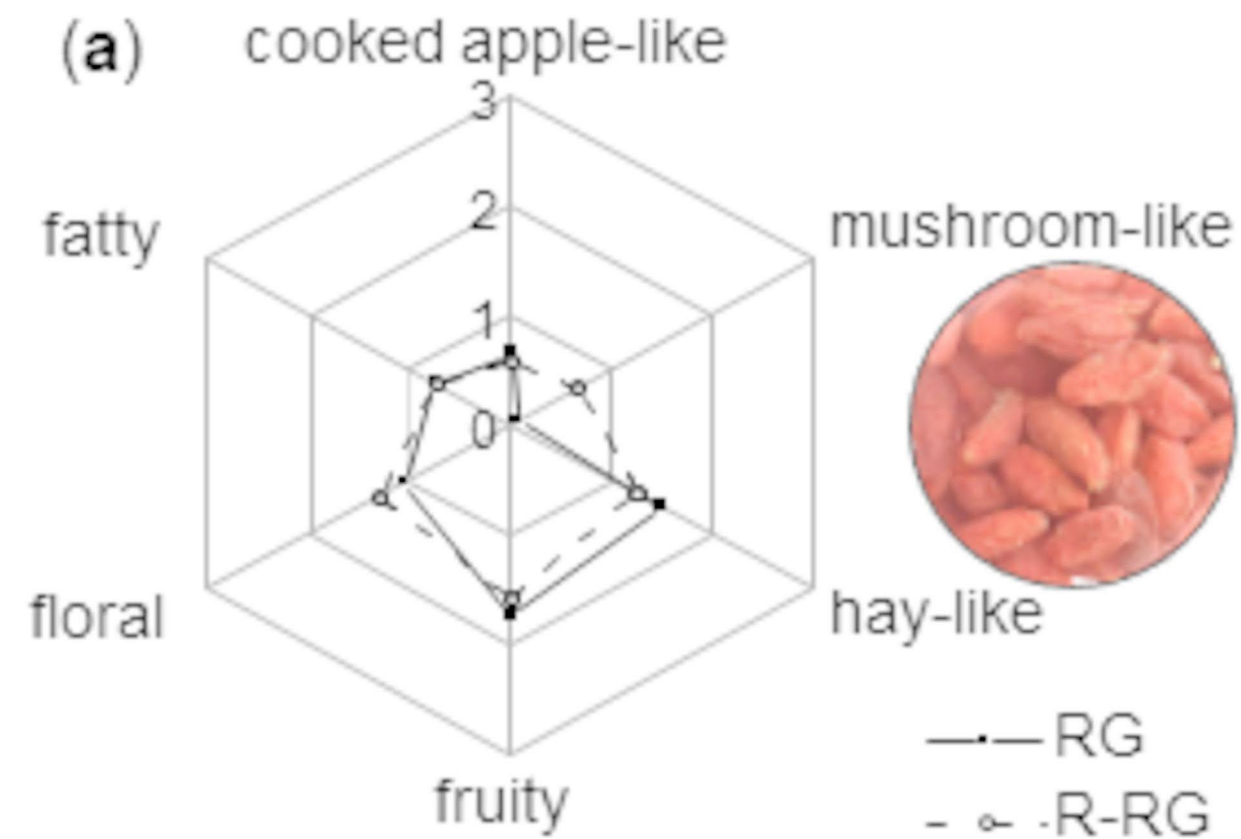


Fig. 2 Radar charts of aroma profiles of **a** commercially dried red goji berries (RG) and **b** commercially dried black goji berries (BG) (in solid line), and their respective reconstitutions (R-RG and R-BG) (in dash line)

Aroma decoding of commercially dried red and black goji berries

Identification of odor-active compounds in commercially dried red goji berries

A drop of the distillate of commercially dried red goji berries on filter paper exhibited the overall smell of commercially dried red goji berries, as agreed by panelists ($n \geq 3$) after the solvent evaporation. It showed *via* GC/O that 45 odor-active areas were found in commercially dried red goji berries. Fourteen of the 45 odor-active areas had FD factors of 32–4096 in DB-FFAP capillary column (Fig. 3a), including seasoning-like and spicy odor note (40), caramel-like (34), fatty, green (23), and vanilla-like, sweet (44), etc. smelling regions. These volatiles were separated into six fractions (AF and NBF1–5) by column chromatography based on their polarities before analysis to prevent a possible co-elution of volatiles during instrumental measurements. Thirteen odor-active compounds were mainly detected in AF (Table 2), and most of the odor-active compounds predominantly occurred in NBF3.

To get the first idea about the odor-active compounds in commercially dried red goji berries, the odor qualities and RIs on polar and nonpolar columns were compared to the data reported in previous publications and recorded in a self-owning database with >200 odor-active compounds. Then, the suggested authentic references were used to compare according to their RIs on both columns, odor qualities, and odor intensity sniffed regarding the heights of the FID signals. Afterward, the odor-active compounds were further qualified by comparing the MS spectrum of the odor-active compounds in the sample with those of the authentic references using GC/MS in full scan mode recorded in MS-EI (Fig. 3b). The odor-active compounds with high FD factors in red goji berries were found as 3-hydroxy-4,5-dimethyl-2(5H)-furanone (40), 4-hydroxy-2,5-dimethyl-3(2H)-furanone (34), (*E, E*)-2,4-nonadienal (23), and vanillin (44) (Table 2).

Identification of odor-active compounds in commercially dried black goji berries

To get a systematic comparison between the two types of goji berries, the amount, workup of extracting, getting the distillate, and concentrated final volume of commercially dried black goji berries were as the same as those of commercially dried red goji berries. The distillate underwent

cAEDA to get a clear difference between these two macroscopic phenotypes according to the obtained FD chromatograms of commercially dried red and black goji berries (Fig. 3c). Three odor-active compounds (4, 8, and 20) in commercially dried red goji berries were undetectable in commercially dried black goji berries.

Twelve odor-active areas showed FD factors of 32–2048 from DB-FFAP capillary column in commercially dried black goji berries (Fig. 3c). The most intensive odor notes were caramel-like (4-hydroxy-2,5-dimethyl-3(2H)-furanone, 34), seasoning-like, spicy (3-hydroxy-4,5-dimethyl-2(5H)-furanone, 40), and vanilla-like, sweet (vanillin, 44).

The aroma classification procedure was suited for the qualification of odor-active volatiles, including the minor compounds in commercially dried black goji berries. The aldehydes dominated in NBF2 and NBF3, and the phenols were mainly detected in NBF5 (Table 2). These data indicated that aroma classification procedure was suitable for the complicate food matrix with goji berries as the examples.

The data from this study was compared with the available literature researching goji berry volatiles (Table 2). It suggested that 11 compounds were first identified in red goji berries. These findings are beneficial from the application of olfactory-assisted identification (GC/O), aroma fractionation, and 2D-GC/MS for getting clear MS spectra of trace or superimposed aroma-active compounds. Previous investigations that studied the volatiles in black goji berries suggested variations in both types and amounts of volatile compounds between commercially dried red and black goji berries [13, 23]. Despite the color and shape differences of both commercially dried red and black goji berries, they shared numerous odor-active compounds in our study, especially the odor-active compounds with high flavor intensities, offering similar notes of caramel-like (e.g. 31, 34), seasoning-like and spicy (e.g. 40), vanilla-like (e.g. 44), and fatty and green (e.g. 17, 23) odor notes. The authentic references of three odor-active compounds, 7, 10, 32, were not commercially available. The identification of these compounds were compared in their odor qualities and RIs to the previous publications and database and compared in their MS spectra with the synthesized references according to the previous descriptions [16], which can be referred for the future studies.

Contents of odor-active components in commercially dried red and black goji berries

The determination of the contents of odor-active compounds was accomplished *via* the SAFE technique and internal standards. Four of the important odor-active compounds (21, 22, 43, 44) with $FD \geq 32$ were precisely quantitated

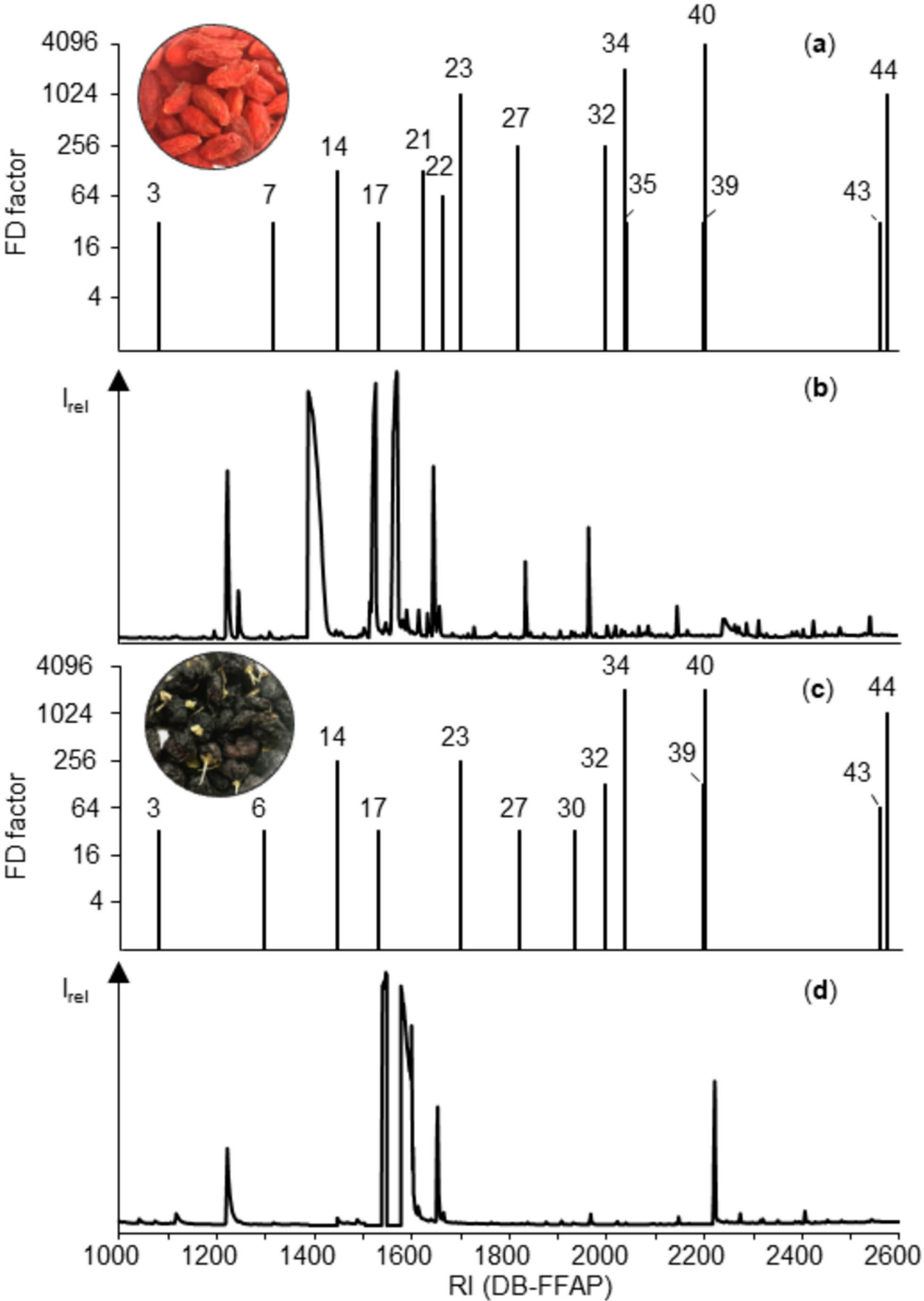


Fig. 3 **a** Flavor dilution (FD) chromatogram and **b** GC/MS chromatogram (full scan mode m/z 35–300) of the distillates obtained by extraction/SAFE distillation of commercially dried red goji berries. **c** Flavor dilution (FD) chromatograms and **d** GC/MS chromatograms (full scan mode m/z 35–300) of the SAFE distillates commercially dried black goji berries. (odor-active compounds with $RI \geq 1000$ and FD factors ≥ 32 are displayed) (numbers refer to Table 2)

using the corresponding isotopically labeled references as the internal standards.

The results (Table 3) revealed that acetic acid (**14**, vinegar-like, 26,300 $\mu\text{g/kg}$), hexanoic acid (**28**, sweaty, 1490 $\mu\text{g/kg}$), butanoic acid (**21**, sweaty, 619 $\mu\text{g/kg}$), (*E*)-2-nonenal (**17**, fatty, green, 410 $\mu\text{g/kg}$), and pentanoic acid (**25**, sweaty, fruity, 244 $\mu\text{g/kg}$) were the predominant odor-actives in commercially dried red goji berries. Chen *et al.* reported that acetic acid was the most abundant volatile (48% of total volatile content) in commercially dried red goji berries [8], which was consistent with our study. Hexanoic acid and pentanoic acid were also previously found in high amounts in red goji berries [10]. Furthermore, high amounts were also found in maltol (**31**, caramel-like, 122 $\mu\text{g/kg}$), 2-phenylethanol (**29**, floral, honey-like, 109 $\mu\text{g/kg}$), and vanillin (**44**, vanilla-like, sweet, 104 $\mu\text{g/kg}$).

With consistency in commercially dried red goji berries, acetic acid (**14**, vinegar-like, 19,900 $\mu\text{g/kg}$) was the predominant odor-active compound in commercially dried black goji berries. The odor-active compounds with high amounts were assigned as maltol (**31**, caramel-like, 472 $\mu\text{g/kg}$), 2-phenylethanol (**29**, floral, violet-like, 462 $\mu\text{g/kg}$), and decanal (**15**, soapy, citrus-like, 218 $\mu\text{g/kg}$). These constituents were more abundant in commercially dried black goji berries than in commercially dried red goji berries.

The trace compounds, 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (**34**, caramel-like, ~1.96–3.90 $\mu\text{g/kg}$), 2-phenylethyl acetate (**26**, honey-like, floral, ~0.69–1.12 $\mu\text{g/kg}$), 3-hydroxy-4,5-dimethyl-2(5*H*)-furanone (**40**, seasoning-like, spicy, ~3.27–4.59 $\mu\text{g/kg}$). These constituents were identified in our study for the first time. The synthesized *trans*-4,5-epoxy-(*E*)-2-decenal was used after determining its synthesized concentration in stock solution (Table S1) and the authentic reference was first used for the identification and quantitation in goji berries.

OAVs of odor-active compounds in commercially dried red and black goji berries

The importance of odor-active compounds in the water matrix was calculated by the content determined in goji berry samples divided by its OT in the water matrix and evaluated as OAV. OAV suggests the contribution of odor-active compounds to the overall aroma profile. Compounds with $\text{OAV} > 1$ indicate they have the potential to be selected as the key aroma in food. The contents of 23 odor-active

compounds surpassed their OTs in commercially dried red goji berries (Table 3). (*E*)- β -Damascenone, evoked a cooked apple-like smell and presented the highest OAV (13,000), followed by a mushroom-like odor impression (1-octen-3-one, 1300), a fatty odor impression ((*E*)-2-nonenal, 1640, (*E*, *E*)-2,4-nonadienal, 240), and a floral odor impression ((*E*)- β -ionone, 190) in red goji berries. With the high OAV (120), ethyl 3-methylbutanoate probably played a crucial role in the fruity-smelling note for red goji berries. Compared to the previous investigation [10], only 18 odor-active compounds, fewer compared with our finding, were determined $\text{OAV} > 1$ in red goji berries. Whereas 19 odor-active compounds determined $\text{OAVs} > 1$ in black goji berries were considered to influence the aroma profile of black goji berries. High OAVs was obtained for 1-octen-3-one (620), (*E*)-2-nonenal (180), and (*E,E*)-2,4-nonadienal (120), which played critical roles in the mushroom-like and fatty smells of black goji berries. Ethyl 3-methylbutanoate (OAV 180) and (*E*)- β -ionone (OAV 390) were regarded as the key fruity and floral odor contributors to black goji berries.

In our study, more odor-active compounds with $\text{OAVs} > 1$ were detected in red goji berries than in black goji berries. The odor-active compounds with high OAVs also evoked a stronger smell in red goji berries than in black goji berries. These differences might result from complicated reasons, such as the precursors and growth conditions (see Section “[Comparison of the key odor-active compounds in commercially dried red and black goji berries](#)”).

Aroma reconstitution

APA and cAEDA data initially reflected the correlations between the aroma profiles of commercially dried red and black goji berries. After further identification and quantitation experiments, the odor-active compounds were more detailed and estimated by calculating OAVs. The OAV data indicated six backbone flavor descriptors were dominated in commercially dried red and black goji berries, i.e., cooked apple-like, fatty, floral, fruity, hay-like, and mushroom-like. All compounds with $\text{OAVs} > 1$ were prepared in the determined concentrations in the aroma reconstitution. They supported the aroma reconstitution for substantiation of the obtained data in this study (Fig. 2) that the compounds with $\text{OAVs} > 1$ were assigned as key odor-active compounds in both berries. The most intensive odor quality was fruity in red and black goji berries reconstitutions. Cooked apple-like and fruity odor attributes in reconstitutions were similar to their original samples, but hay-like odor attribute was weaker in both aroma reconstitutions. Mushroom-like odor note was the only odor note that was judged significantly stronger (*t*-test, TDIST function in Microsoft Excel, $p < 0.05$) in red goji berries reconstitutes than the original

red goji berries. Even though the aroma recombination has many limitations in replicating the original complexity regarding the complicated food matrix, the aroma recombination results verified compounds with OAVs > 1 as the key odor-active compounds in commercially dried red and black goji berries.

Comparison of the key odor-active compounds in commercially dried red and black goji berries

Two typical C₁₃-norisoprenoids, (*E*)- β -damascenone and (*E*)- β -ionone, are reported as the key odor-active compounds in fruits such as raspberries [30] and apricots [17]. In particular, (*E*)- β -damascenone is rich in *Lycium* plants, and its glucosidic precursor was isolated and analyzed in *Lycium* plants [31]. C₁₃-norisoprenoids are known to be formed from carotenoids. Specifically, neoxanthin was reported as the precursor of β -damascenone, and β -carotene was the precursor of β -ionone in fruit [32]. To our knowledge, red goji berries are rich in carotenoids (~5.9–11 mg GAE/g FW), while black goji berries are lack of carotenoids (~0.40 mg GAE/g FW) [5]. Neoxanthin and β -carotene were ~9.6–59 μ g/g DW and 80–410 μ g/g DW, respectively, in red goji berries [5]. While these carotenoids accounted for ~270 and ~19 μ g/g DW in black goji berries [5]. Previous investigations reported that carotenoids could be biosynthesized in both types of goji berries, but black goji berries cannot develop the chromoplast, which stores most carotenoids [4]. It causes carotenoids to be continuously degraded and little to accumulate in black goji berries [4]. Although the drying process impacts the lipids little, C₁₃-norisoprenoids' content accumulates through enzymatic reduction and glycosylation in acidic media [32].

With mushroom-like and fatty odor impressions, 1-octen-3-one, (*E*)-2-nonenal, and (*E,E*)-2,4-nonadienal were assigned as the crucial aroma-active components in both red and black goji berries (Fig. 4). These compounds are mainly formed from unsaturated fatty acids, such as palmitoleic acid (16:1*n*-7, possible precursor of (*E*)-2-nonenal), linoleic acid (18:2*n*-6, possible precursor of 1-octen-3-one and (*E*)-2-nonenal), linolenic acid (18:3*n*-3, possible precursor of (*E,E*)-2,4-nonadienal), and arachidonic acid (20:4, possible precursor of 1-octen-3-one and (*E*)-2-nonenal), by autooxidation, photooxidation, or enzymatic oxidation [33–35]. Although the fatty acids patterns were reported quite similar in both types, less fatty acids contents were in red goji berries compared to black goji berries [2, 36]. While the OAV data suggested that these fatty acid derivatives were more pronounced in red goji berries than in black goji berries (Table 3).

The fruity odor impression in red and black goji berries was mainly represented by ethyl 3-methylbutanoate, which

was generated from the amino acid (i.e. leucine) and the responding branched short-chain fatty acid (i.e. 3-methylbutanoic acid) in fruit [37, 38]. The contents and OAV data indicated that ethyl 3-methylbutanoate and 3-methylbutanoic acid were slightly more pronounced in black goji berries than in red goji berries.

Conclusion

Combining instrumental analysis with the human sensory system is more sensitive than instrumental detectors. SAFE resulted in a relatively comprehensive extraction of volatile, GC/O was beneficial for the perception of the compounds with low OTs, and aroma fractionation and 2D-GC/MS were useful for getting the clear MS spectra for the identification. These promoted the detection of 45 odor-active compounds in commercially dried red and black goji berries. Among these, 11 compounds (2, 24, 26, 31, 32, 34, 35, 40, 43–45) were first reported as goji berry components in our study, and 11 compounds (3, 14, 17, 23, 27, 32, 34, 39, 40, 43, 44) were with high FD factors (≥ 32) in both commercially dried red and black goji berries. The (semi-)quantitation results showed more abundant odor-active compounds in red goji berries than in black goji berries. The OAV data reflected that 23 and 20 odor-active compounds surpassed their OTs in commercially dried red and black goji berries, respectively. The aroma profile of red goji berries was similar but stronger than the aroma profile of black goji berries. The evident variations in the presence of lipid derivatives were detected in both types of goji berries.

Aroma fractionation has the potential to enrich trace compounds and separate co-eluting compounds. It can offer the reference for further flavor analysis and an economic choice that gets rid of the expensive precise and advanced instruments for aroma analysis (e.g. gas chromatography with ion mobility spectrometry, time-of-flight, Orbitrap analyzers, or tandem mass spectrometry). Many studies on goji aroma have focused on the volatiles [7, 8, 10, 11, 12, 13, 23, 26, 25], most of which contribute little on the overall aroma profile. Utilizing the human olfactory sense to distinguish odor-active compounds can effectively prevent the omission of trace but crucial compounds, such as the ones synthesized (7, 10, 32) and identified for the first time (2, 24, 26, 31, 32, 34, 35, 40, 43–45) in this study. The analysis will be going on the fresh and dried goji berries with different processing methods to provide more information on the food quality and control for the goji market.

Table 2 The odor qualities, retention indices (RIs), flavor dilution (FD) factors, and the eluted fractions of odor-active compounds in commercially dried red and black goji berries

No. ^a	Compound	Odor quality	RI ^b		FD factor ^c		Fraction ^d	Lit. ^e
			DB-5	FFAP	RG	BG		
1	Ethyl 2-methylbutanoate	Fruity	847	1049	2	2	AF	v
2	Ethyl 3-methylbutanoate	Fruity, blueberry-like	853	1066	2	8	NBF3	
3	Hexanal	Green, grassy	802	1078	32	32	NBF3	i, ii, iii, v,vi, vii, viii, x
4	Unknown ^f	Malty, sweaty		1149	2		NBF2	
5	Octanal	Citrus-like, green	1004	1283	16	2	NBF3	ix, x
6	1-Octen-3-one	Mushroom-like	978	1295	16	32	NBF2	iii, vii, x
7	2-Acetyl-1-pyrroline ^g	Popcorn-like, roasty	909	1314	32	16	NBF5	
8	(<i>E</i>)-2-Heptenal ^g	Green, fatty	958	1319	2		NBF2	ii
9	Nonanal	Citrus-like, soapy	1106	1386	1	4	NBF3	vii, ix
10	2-Propionyl-1-pyrroline ^g	Popcorn-like, roasty	1021	1410	2	1	NBF5	
11	Ethyl cyclohexanecarboxylate ^g	Fruity, sweet	1136	1414	4	8	NBF2	
12	(<i>E</i>)-2-Octenal	Fatty, nutty	1060	1425	8	1	NBF3	i, vi, vii, x
13	2-Ethyl-3,5-dimethylpyrazine ^g	Earthy	1077	1436	2	4	NBF3	
14	Acetic acid	Vinegar-like		1444	128	256	AF	i, ii, vi ix
15	Decanal	Soapy, citrus-like	1208	1491	16	16	NBF3	iii, v,vii
16	3-Isobutyl-2-methoxypyrazine ^g	Earthy, green bell pepper-like	1177	1516	16	4	NBF3	
17	(<i>E</i>)-2-Nonenal	Fatty, green	1161	1529	32	32	NBF3	iii, iv, vi, vii
18	Linalool	Citrus-like, floral	1112	1536	1	2	NBF4	iii, iv, vii, x,xi
19	(<i>E, Z</i>)-2,6-Nonadienal ^g	Cucumber-like	1155	1581	4	16	NBF2	i, vii, x
20	2-Acetylpyridine	Roasty	1034	1601	1		NBF4	iii
21	Butanoic acid	Sweaty	<800	1621	128	1	AF	i, vi, x
22	2-, and 3-Methylbutanoic acid	Sweaty	841	1662	64	16	AF	iii, v,vi, xii
23	(<i>E,E</i>)-2,4-Nonadienal	Fatty, green	1218	1697	1024	256	NBF2	xii
24	3-Methyl-2,4-nonanedione	Hay-like, aniseed-like, fish-like	1262	1715	4	16	NBF5	
25	Pentanoic acid	Sweaty, fruity	881	1731	2	2	AF	v, vii
26	2-Phenylethyl acetate	Honey-like, floral	1256	1816	4	4	NBF3	xiii
27	(<i>E</i>)- β -Damascenone	Cooked apple-like	1382	1817	256	32	NBF2	x
28	Hexanoic acid	Sweaty	980	1838	8	2	AF	i, vi, vii, x,xii
29	2-Phenylethanol	Floral, honey-like	1115	1908	4	2	NBF5	i, ii, iii, xi
30	(<i>E</i>)- β -Ionone	Floral, violet-like	1483	1933	16	32	NBF4	ii, iv, vi, xi, xii
31	Maltol	Caramel-like	1128	1966	8	16	AF	
32	<i>trans</i> -4,5-Epoxy-(<i>E</i>)-2-decenal	Metallic	1382	1993	256	128	NBF4	
33	Phenol	Ink-like, phenolic	975	2005	8	1	NBF4	xiv
34	4-Hydroxy-2,5-dimethyl-3(2 <i>H</i>)-furanone	Caramel-like	1158	2033	2048	2048	AF	
35	γ -Nonalactone	Coconut-like	1362	2033	32	16	NBF5	
36	Octanoic acid	Carrot-like, musty	1166	2053	4	2	AF	iii
37	<i>m</i> -Cresol	Smoky, phenolic	1130	2089	1	8	NBF5	x
38	Eugenol	Clove-like	1357	2166	1	1	NBF4	x
39	2-Methoxy-4-vinylphenol	Smoky, clove-like	1311	2197	32	128	NBF5	iii, vi
40	3-Hydroxy-4,5-dimethyl-2(5 <i>H</i>)-furanone	Seasoning-like, spicy	1100	2198	4096	2048	AF	
41	γ -Undecalactone	Peach-like	1576	2262	1	2	NBF5	x
42	Decanoic acid	Soapy, musty	1360	2266	2	8	AF	i, x
43	Phenylacetic acid	Honey-like, beeswax-like	1241	2561	32	64	AF	

Table 2 (continued)

No. ^a	Compound	Odor quality	RI ^b		FD factor ^c		Fraction ^d	Lit. ^e
			DB-5	FFAP	RG	BG		
44	Vanillin	Vanilla-like, sweet	1401	2572	1024	1024	AF	
45	3-Phenylpropanoic acid	Floral, cinnamon-like	1346	2629	4	2	AF	

^aThe order of the odor-active compounds was according to the elution order on DB-FFAP column

^bRetention index; each RI was calculated based on the retention times and carbon atoms of adjacent alkane references

^cFD factor, flavor dilution factor; RG, red goji berry; BG, black goji berry

^dFractionation was carried out on the water-cooled column chromatography

^eThe odor-active compounds were reported in goji berries in the listed literature; i [22],; ii [11],; iii [7],; iv [23],; v [13],; vi [24],; vii [10],; viii [25],; ix [8],; x [12],; xi [26],; xii [27],; xiii [28],; xiv [29]

^fOdor-active compounds only can be perceived on sniffing port, no available references or MS spectrums for further identification in our study

^gOdor-active compounds can only be identified by comparing the odor quality and RIs on both DB-5 and DB-FFAP columns to the authentic references, the low MS signal was unable to get a clear spectrum in our study

Table 3 The contents, relative standard deviations (RSD), odor thresholds (OTs), and odor activity values (OAVs) of the odor-active compounds measured in commercially dried red goji berries (RG) and commercial dried black goji berries (BG)

Compound	Content (µg/kg) ^a		RSD % ^b		OT (µg/kg) ^c	OAV ^d	
	RG	BG	RG	BG		RG	BG
(<i>E</i>)- β -Damascenone	76.2		12		0.006	13,000	
(<i>E</i>)-2-Nonenal	410	46.2***	11	14	0.25	1640	180
1-Octen-3-one	20.2	9.88***	8	5	0.016	1300	620
(<i>E,E</i>)-2,4-Nonadienal	15.1	7.24**	10	10	0.062	240	120
(<i>E</i>)- β -Ionone	4.03	8.11**	11	6	0.021	190	390
Ethyl 3-methylbutanoate	2.83	3.64*	14	7	0.023	120	160
3-Methyl-2,4-nonanedione	4.66		28		0.046	101	
Acetic acid	263,000	199,000**	5	13	5600	47	36
Linalool	1.37	5.53**	5	12	0.087	16	64
<i>trans</i> -4,5-Epoxy-(<i>E</i>)-2-decenal	2.7	2.21	10	2	0.22 ^e	12	10
Decanoic acid	33.4	26.2*	4	13	3.5 ^e	10	7
Decanal	84.1	219***	14	4	9.3	9	24
γ -Undecalactone	9.83	20.8***	6	2	2.1	5	10
Nonanal	11.4	25.3**	9	15	2.8	4	9
Hexanal	8.44	11.1*	12	9	2.4	4	5
2-Acetylpyridine	9.73		8		3.9 ^e	2	
γ -Nonalactone	21.1	23.2	3	9	9.7	2	2
Vanillin	104	15.5***	6	13	53	2	<1
3-Hydroxy-4,5-dimethyl-2(5 <i>H</i>)-furanone	3.27	4.59**	15	0	1.7	2	3
2-Methoxy-4-vinylphenol	25.5	29.7	10	14	21 ^e	1	1
Eugenol	2.08	2.80**	11	1	1.8	1	2
Octanoic acid	200	37.1***	5	12	190	1	<1
Octanal	3.48	6.43**	9	11	3.4	1	2
2-Phenylethanol	109	462***	2	12	140	<1	3
Butanoic acid	619	157***	7	9	1000	<1	<1
Phenylacetic acid	37.7	35.7	8	2	68	<1	<1
Hexanoic acid	1490	191***	13	12	4800	<1	<1
<i>m</i> -Cresol	4.17	11.0***	12	7	15	<1	<1
2-, and 3-methylbutanoic acid	72.7	41.7***	7	6	490	<1	<1
3-Phenylpropanoic acid	9.61	11.2**	7	1	120	<1	<1
4-Hydroxy-2,5-dimethyl-3(2 <i>H</i>)-furanone	1.96	3.90*	3	14	25	<1	<1
Maltol	122	472***	12	5	5000	<1	<1
Pentanoic acid	244	82.0***	4	14	11,000	<1	<1
Phenol	28.3	120***	14	14	3400 ^e	<1	<1
2-Phenylethyl acetate	0.668	1.12**	2	12	360	<1	<1

^aThe contents of odor-active compounds were average in 2–4 experiments; * indicated that the significant difference between RG and BG with $p < 0.05$; ** indicated that the significant difference between RG and BG with $p < 0.01$; *** indicated that the significant difference between RG and BG with $p < 0.001$

^bRSD relative standard deviations

^cOdor thresholds (OTs) in water matrix were obtained from the Leibniz database: <https://www.leibniz-lsb.de/datenbanken/leibniz-lsb-tum-odorant-database/odorantdb/>

^dOdor activity values (OAVs) of odor-active compounds were the ratios of the concentrations and the corresponding OTs

^eThe odor thresholds (OTs) were from the in-house database in our institute in the water matrix

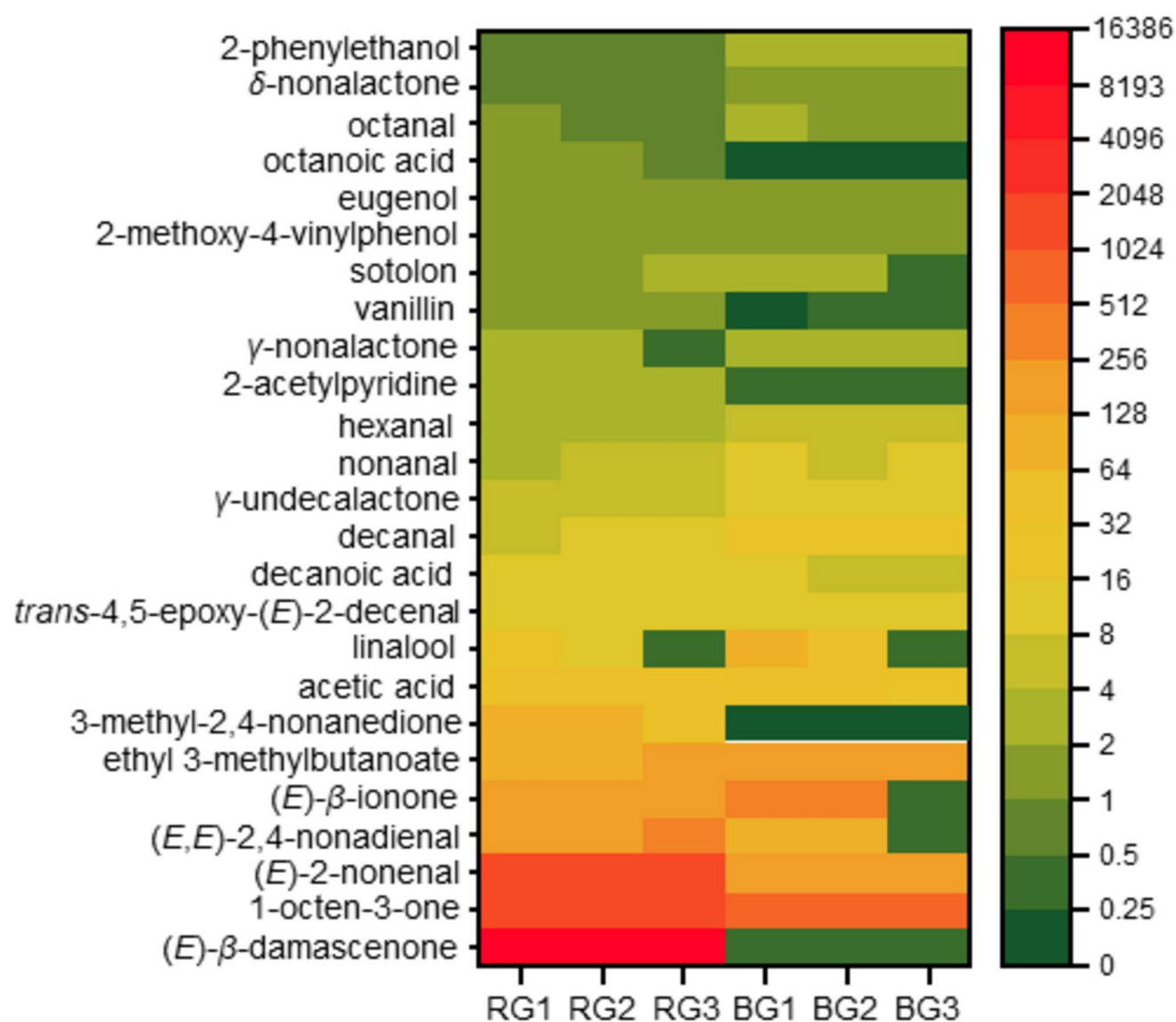


Fig. 4 Heatmap of the OAVs of odor-active compounds in red goji berry samples (RG1-3) and black goji berry samples (BG1-3)

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s00217-025-04745-7>.

Acknowledgements Kindly acknowledgment was given to the Department of Food Chemistry and Analytical Chemistry (170a) and the Department of Flavor Chemistry (150h) for their general help and instrumental support. Many thanks were given to Sarah Kramp, Katharina Schuster, and Jonathan Schäfer for their tremendous knowledge of biosynthesis pathways, chemical synthesis, and data analysis. Special thanks were given to the late Prof. Dr. Michael Granvogl for his initial idea and strong support of this work. We deeply miss him.

Author contributions Yan.Z. did the experiments, wrote the main manuscript text, and prepared tables and figures. C.O. provided a working place, materials, chemicals, references, and instruments, etc. M.G. provided a working place, materials, chemicals, references, instruments, etc., and provided initial supervision. Yanyan.Z. provided materials, chemicals, instruments, etc., and provided supervision. Yan.Z., C.O., L.Z., Y.L., Y.C., X.F., W.W., and Yanyan.Z. reviewed the manuscript.

Funding Open Access funding enabled and organized by Projekt DEAL.

This research did not receive any specific grant from funding agencies in the public, commercial, or not-for-profit sectors.

Data availability The raw datasets generated during the current study are available from the corresponding author on reasonable request.

Declarations

Conflict of interests The authors declare no competing interests.

Ethical approval and consent to participate The sensory evaluation in our study strictly and seriously followed the ethical and professional practice of our group regulation and was performed with the approval of the Ethics Committee of the University of Hohenheim (applied in April 2024, no case number available, and approved on 16th May 2024). All participants were fully and comprehensively informed about the course, purpose, and the relevant risks of the study. The au-

thor confirmed that all participants' rights, privacy, and voluntariness were protected during the research. All participants agreed in writing to participate voluntarily in the sensory analysis and had the right to withdraw from the study at any time. The author announced that there was no force to participate and no release of participant data without their knowledge.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons licence, and indicate if changes were made. The images or other third party material in this article are included in the article's Creative Commons licence, unless indicated otherwise in a credit line to the material. If material is not included in the article's Creative Commons licence and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this licence, visit <http://creativecommons.org/licenses/by/4.0/>.

References

- Yao R, Heinrich M, Weckerle CS (2018) The genus *Lycium* as food and medicine: a botanical, ethnobotanical and historical review. *J Ethnopharmacol* 212:50–66. <https://doi.org/10.1016/j.jep.2017.10.010>
- Wang Q, Zeng S, Wu X et al (2018) Interspecies developmental differences in metabonomic phenotypes of *Lycium ruthenicum* and *L. barbarum* fruits. *J Proteome Res* 17:3223–3236. <https://doi.org/10.1021/acs.jproteome.8b00349>
- Potterat O (2010) Goji (*Lycium barbarum* and *L. chinense*): phytochemistry, pharmacology and safety in the perspective of traditional uses and recent popularity. *Planta Med* 76:7–19. <https://doi.org/10.1055/s-0029-1186218>
- Liu Y, Zeng S, Sun W et al (2014) Comparative analysis of carotenoid accumulation in two goji (*Lycium barbarum* L. and *L. ruthenicum* Murr.) fruits. *BMC Plant Biol* 14:269. <https://doi.org/10.1186/s12870-014-0269-4>
- Zhang Q, Chen W, Zhao J et al (2016) Functional constituents and antioxidant activities of eight Chinese native goji genotypes. *Food Chem* 200:230–236. <https://doi.org/10.1016/j.foodchem.2016.01.046>
- Zeng S, Wu M, Zou C et al (2014) Comparative analysis of anthocyanin biosynthesis during fruit development in two *Lycium* species. *Physiol Plant* 150:505–516. <https://doi.org/10.1111/ppl.12131>
- Kim JS, Chung HY (2009) GC-MS analysis of the volatile components in dried Boxthorn (*Lycium chinensis*) fruit. *J Appl Biol Chem* 52:516–524. <https://doi.org/10.3839/jksabc.2009.088>
- Chen F, Su Y, Zhang F et al (2015) Low-temperature headspace-trap gas chromatography with mass spectrometry for the determination of trace volatile compounds from the fruit of *Lycium barbarum* L. *J Sep Sci* 38:670–676. <https://doi.org/10.1002/jssc.201400862>
- Dunkel A, Steinhaus M, Kotthoff M et al (2014) Nature's chemical signatures in human olfaction: a foodborne perspective for future biotechnology. *Angew Chem Int Ed Engl* 53:7124–7143. <https://doi.org/10.1002/anie.201309508>
- Lu J, Li H, Quan J et al (2017) Identification of characteristic aroma volatiles of Ningxia Goji berries (*Lycium barbarum* L.) and their developmental changes. *Int J Food Prop* 20:S214–S227. <https://doi.org/10.1080/10942912.2017.1295254>
- Lee GH, Shin Y, Oh MJ (2008) Aroma-active components of *Lycii fructus* (kukija). *J Food Sci* 73. <https://doi.org/10.1111/j.1750-3841.2008.00851.x>. C500-5
- Wang S, Su Q, Zhu Y et al (2024) Sensory-guided establishment of sensory lexicon and investigation of key flavor components for goji berry pulp. *Plants (Basel)* 13. <https://doi.org/10.3390/plants13020173>
- Zhou Y, Wang D, Duan H et al (2023) Detection and analysis of volatile flavor compounds in different varieties and origins of goji berries using HS-GC-IMS. *LWT* 187:115322. <https://doi.org/10.1016/j.lwt.2023.115322>
- Cui C, Zhao D, Huang J et al (2022) Progress on research and development of goji berry drying: a review. *Int J Food Prop* 25:435–449. <https://doi.org/10.1080/10942912.2022.2046054>
- Schieberle P, Hofmann T (2011) Mapping the combinatorial code of food flavors by means of molecular sensory science approach. In: CRC Press (eds), *Food Flavor*, pp 413–438. <https://doi.org/10.1201/b11187-19>
- Kiefl J, Pollner G, Schieberle P (2013) Sensomics analysis of key hazelnut odorants (*Corylus avellana* L. 'Tonda Gentile') using comprehensive two-dimensional gas chromatography in combination with time-of-flight mass spectrometry (GC×GC-TOF-MS). *J Agric Food Chem* 61:5226–5235. <https://doi.org/10.1021/jf400807w>
- Greger V, Schieberle P (2007) Characterization of the key aroma compounds in apricots (*Prunus armeniaca*) by application of the molecular sensory science concept. *J Agric Food Chem* 55:5221–5228. <https://doi.org/10.1021/jf0705015>
- Engel W, Bahr W, Schieberle P (1999) Solvent assisted flavour evaporation - a new and versatile technique for the careful and direct isolation of aroma compounds from complex food matrices. *Eur Food Res Technol* 237–241. <https://doi.org/10.1007/s002170050486>
- Zhai X, Granvogl M (2019) Characterization of the key aroma compounds in two differently dried *Toona sinensis* (A. Juss.) Roem. By means of the molecular sensory science concept. *J Agric Food Chem* 67:9885–9894. <https://doi.org/10.1021/acs.jafc.8b06656>
- Zheng Y, Oellig C, Zhang Y et al (2024) Characterization of the key odorants in goji wines in three levels of sweetness by applications of sensomics approach. *Food Chem*:140803. <https://doi.org/10.1016/j.foodchem.2024.140803>
- Grosch W (1993) Detection of potent odorants in foods by aroma extract dilution analysis. *Trends Food Sci Technol* 4:68–73. [https://doi.org/10.1016/0924-2244\(93\)90187-F](https://doi.org/10.1016/0924-2244(93)90187-F)
- Ryu SN, Kim SM (1998) Volatile oil composition of Boxthorn (*Lycium chinense* M.) leaves. *Korean J Crop Sci* 43:189–193
- Altintas A, Kosar M, Kirimer N et al (2006) Composition of the essential oils of *Lycium barbarum* and *L. ruthenicum* fruits. *Chem Nat Compd* 42:24–25. <https://doi.org/10.1007/s10600-006-0028-3>
- Xie L, Mujumdar AS, Zhang Q et al (2017) Pulsed vacuum drying of wolfberry: effects of infrared radiation heating and electronic panel contact heating methods on drying kinetics, color profile, and volatile compounds. *Dry Technol* 35:1312–1326. <https://doi.org/10.1080/07373937.2017.1319854>
- Chung IM, Nagella P, Ahn YS et al (2011) Composition of the essential oil and petroleum ether extract of *Lycium chinense* miller fruits and antioxidant activity of its several extracts. *J Med Plant Res* 5:5973–5981. <https://doi.org/10.5897/JMPR11.285>
- Sannai A, Fujimori T, Kato K (1983) Neutral volatile components of 'kukoshi' (*Lycium chinense* M.). *Agric Biol Chem* 47:2397–2399. <https://doi.org/10.1271/bbb1961.47.2397>
- Kim SY, Lee KH, Chang KS et al (1997) Taste and flavor compounds in box thorn (*Lycium Ckinense* Miller) leaves. *Food Chem* 58:297–303. [https://doi.org/10.1016/S0308-8146\(96\)00099-4](https://doi.org/10.1016/S0308-8146(96)00099-4)

28. Choi SH (2014) Flavor components in dried fruit of the Chinese matrimony vine during storage. *J Life Sci* 24:1325–1329. <https://doi.org/10.5352/JLS.2014.24.12.1325>
29. Oğuz İ, Oğuz Hİ, Ürün İ et al (2023) Determination of aroma and protein contents in organic *Lycium barbarum* L. and *Lycium chinense* miller fruits in different ripening periods. *Erwerbs-Obstbau* 65:1171–1183. <https://doi.org/10.1007/s10341-022-00775-7>
30. Lang S, Ozcelik M, Kulozik U et al (2020) Processing of raspberries to dried fruit foam: impact on major odorants. *Eur Food Res Technol* 246:2537–2548. <https://doi.org/10.1007/s00217-020-03595-9>
31. Näf R, Velluz A, Thommen W (1990) Isolation of a glucosidic precursor of damascenone from *Lycium halimifolium* Mil. *Tetrahedron Lett* 31:6521–6522
32. Rienth M, Vigneron N, Darriet P et al (2021) Grape berry secondary metabolites and their modulation by abiotic factors in a climate change scenario - a review. *Front Plant Sci* 12:643258. <https://doi.org/10.3389/fpls.2021.643258>
33. Lin J, Blank I (2003) Odorants generated by thermally induced degradation of phospholipids. *J Agric Food Chem* 51:4364–4369. <https://doi.org/10.1021/jf034300m>
34. Wang C, Chin CK, Ho CT et al (1996) Changes of fatty acids and fatty acid-derived flavor compounds by expressing the yeast Δ -9 desaturase gene in tomato. *J Agric Food Chem* 44:3399–3402. <https://doi.org/10.1021/jf960174t>
35. Tsuzuki S (2019) Higher straight-chain aliphatic aldehydes: importance as odor-active volatiles in human foods and issues for future research. *J Agric Food Chem* 67:4720–4725. <https://doi.org/10.1021/acs.jafc.9b01131>
36. Zheng Y, Lehnert K, Vetter W (2025) The high share of Steryl esters is responsible for the unusual sterol pattern of black goji berries. *J Food Compost Anal* 106921. <https://doi.org/10.1016/j.jfca.2024.106921>
37. Matich A, Rowan D (2007) Pathway analysis of branched-chain ester biosynthesis in apple using deuterium labeling and enantioselective gas chromatography-mass spectrometry. *J Agric Food Chem* 55:2727–2735. <https://doi.org/10.1021/jf063018n>
38. Rettberg N, Thörner S, Labus AB et al (2014) Aroma active monocarboxylic acids - origin and analytical characterization in fresh and aged hops. *Brewing Sci* 67:33–47

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.