



Effect of cooking on aroma profile of red kidney beans (*Phaseolus vulgaris*) and correlation with sensory quality



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ABSTRACT

Volatile aroma compounds of three varieties of red kidney beans (*Phaseolus vulgaris*) namely Kashmiri red, Sharmili and Chitra were extracted in raw state using solid-phase microextraction (SPME) and cooked state using simultaneous distillation extraction (SDE). During cooking a significant ($p < 0.05$) reduction in the content of several aldehydes, alcohols and terpene hydrocarbons while an increase in content of various sulfurous compounds, terpene alcohols, ketones and pyrazines was noted. Descriptive sensory analysis showed that the maximum intensity of 'kidney bean', 'earthy' and 'smoky' odour was observed in Kashmiri red while Sharmili variety was characterised by 'sulfurous' odour. Correlation of volatile profile data with descriptive sensory analysis and odour activity values clearly established the role of compounds, such as methanethiol, diethyl sulfide, dimethyl disulfide, methional and dimethyl trisulfide, in contributing to 'cooked kidney bean' aroma, while dimethyl sulfoxide, dimethyl sulfone and ethyl methyl sulfone were responsible for 'sulfurous' aroma.

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1. Introduction

Red kidney beans constitute an important part of the diet worldwide especially for those living in developing and underdeveloped tropical & subtropical areas (Siddiq, Ravi, Harte, & Dolan, 2010). Despite having low digestibility (Shimelis & Rakshit, 2007), they are an important source of proteins in countries having short supply of animal proteins and for vegetarians. They are a good source of calcium, potassium, magnesium, iron and phosphorus (Wang, Hatcher, Tyler, Toews, & Gawalko, 2010). India is ranked second in the world in production of red kidney beans after Myanmar (3.6 million metric tons and 3.8 million metric tons in 2013, respectively; FAOSTAT²). These are commercialised as dry packaged form, canned beans, brine-packed whole beans and bean flour for commercial baking (Economic Research Service, USDA³, 2000).

Apart from being a source of various nutrients, kidney beans impart excellent aroma to food. However, the origin of aroma in red kidney beans has not been thoroughly investigated. Buttery, Seifert, and Ling (1975), performed vacuum and atmospheric distillation of soaked dry beans to determine the volatile compounds

in raw and cooked beans, respectively. 1-Octen-3-ol, 1-hexanol, (*Z*)-5-octen-2-one, (*Z*)-5-octen-2-ol, (*Z*)-3-hexen-1-ol, (*E,E*)-3,5-octadien-2-one, 2,5-dimethyl pyrazine, benzaldehyde and 2-phenylacetaldehyde were reported as major components in raw beans, and thialdine, *p*-vinylguaiacol, thiazole compounds, furans, 3,5-dimethyl-1,2,4-trithiolane and 2-methyl-5-ethylpyridine as major components in cooked beans. In another study conducted by Lovegren, Fisher, Legendre, and Schuller (1979), 2-butanol, 1-pentanol and dimethyl sulfide were identified as major compounds of red kidney beans by direct transfer technique in powdered bean. Van Ruth, Dings, Buhr, and Posthumus (2004) used proton transfer reaction-mass spectrometry for *in vitro* and *in vivo* dynamic release of flavour compounds from canned red kidney beans. Four major spectral fragments had *m/z* values of 33, 45, 59 and 73. Gas chromatography-mass spectrometry (GC-MS) analysis further resulted in the identification of methanol (*m/z* 33), 2-methylbutanal (*m/z* 45), 2,3-butanedione (*m/z* 59), 2-methylpropanal (*m/z* 73) and 2-butanone (*m/z* 73) as major compounds.

In another study carried out by Oomah, Liang, and Balasubramanian (2007), a total of 62 compounds were identified from seven cultivars of raw dry beans using headspace solid-phase microextraction (HS-SPME). In this study, authors studied two cultivars each of pinto and red kidney beans and three cultivars of black beans. Based on high scores in principal component analysis (PCA) and low threshold values, hexanal, (*E,E*)-3,5-octadien-2-one, 1-penten-3-ol and benzaldehyde were

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² <http://faostat.fao.org/site/567/DesktopDefault.aspx?PageID=567#anco>.

³ <http://www.ers.usda.gov/topics/crops/vegetables-pulses/dry-beans.aspx>.

considered as the most important volatile marker compounds of raw beans. In comparison with previous studies significantly higher number of compounds were identified by Oomah et al. (2007) using HS-SPME and GC-MS. Aroma of beans is generated mainly during cooking. However, no studies were carried out by them on the aroma composition of cooked beans.

Although there are several reports on volatile aroma constituents, no studies exist on the effect of cooking on volatile compounds in red kidney beans. Moreover, despite the fact that sensory quality of beans could be mainly due to volatiles generated during cooking, the role of volatiles generated by cooking towards sensory quality has not been fully explored. Therefore, the objective of the present study was to evaluate the effect of cooking on volatile aroma constituents of different varieties of red kidney beans. Correlation of volatile constituents generated during cooking with sensory quality using PCA was also attempted to elucidate their role in imparting characteristic aroma of cooked beans.

2. Materials and methods

2.1. Chemical standards

Diethyl ether (analytical grade reagent) was obtained from SDFCL, Mumbai, India and was double distilled before use. Sodium sulfate was obtained from Chemco Fine Chemicals, India. Analytical standards such as methional, nonanal, hexanal, 6-methyl-5-hepten-2-one, benzothiazole, limonene, isoeugenol, 3-methylbutanal, dimethyl sulfone, 2-ethylfuran, decanal, 2-phenylethyl alcohol, thymol, 2-octanol, (*E*)-2-nonenal, *p*-vinylguaiaicol, acetophenone, dimethyl trisulfide, geranyl acetone, α -terpineol, 2-ethyl-3,5-dimethylpyrazine, dimethyl sulfide, dimethyl disulfide, benzeneacetaldehyde, isoamyl acetate, 1-octen-3-ol and 2,5-dimethylfuran were purchased from Sigma-Aldrich (St. Louis, MO). Ethyl acetate, benzyl alcohol and (*Z*)-3-hexen-1-ol were purchased from SDFCL, Mumbai, India. 3-Methyl-1-butanol was purchased from Reachim, Moscow, Russia. Dimethyl sulfoxide was purchased from Sisco Research Laboratories Pvt. Ltd, Mumbai, India and cuminaldehyde was purchased from Benzochem Industries Pvt. Ltd, Mumbai, India.

2.2. Methods

2.2.1. Isolation of aroma compounds from raw red kidney beans

Three varieties of dry beans, namely Kashmiri red, Sharmili and Chitra, were purchased from a local market, Chembur, Mumbai, India. Beans were harvested in year 2014 and were stored in airtight containers at room temperature (25 ± 2 °C) until further use.

Kidney beans (12.0 g) were mixed with 72 mL distilled water and 1.24 μ g of 2-octanol (15 μ L of 10^4 times diluted in methanol) was then added as an internal standard. The resulting mixture was homogenised using a high speed homogeniser (Mixer B-400; Buchi, Flawil, Switzerland) for 2 min. The resulting slurry was centrifuged (5810 R, Eppendorf AG, Germany) at a speed of 12,000 rpm for 20 min at 10 °C. A 15-mL aliquot of supernatant was transferred to an SPME vial (40 mL, Supelco, USA) and added with 4.5 g NaCl. To extract a wide range of compounds, DVB/CAR/PDMS (divinylbenzene/Carboxen/polydimethylsiloxane; Supelco, Bellefonte, PA) fibre was used. To extract the maximum number of volatile constituents, SPME extraction conditions were optimised. Samples were equilibrated for 1 h with magnetic stirring before extraction. For equilibration and extraction, four different temperatures, i.e. 30, 40, 50 and 60 °C, were studied. At each temperature the extraction was carried out for three different times, 15, 30 and 45 min. Compounds identified at each extraction time and temperature are shown in Table S1 (supplementary information). The highest number of compounds (50) and total volatile concentration

(1.76 mg kg⁻¹) was obtained at 50 °C and 30 min. After extraction, the fibre was desorbed (270 °C) in the injection port of a GC-MS for 5 min to identify the compounds.

2.2.2. Isolation of aroma compounds from cooked red kidney beans

To simulate cooking conditions and extract aroma constituents of cooked beans, simultaneous distillation extraction (SDE) was employed. The SDE isolate contains compounds generated specifically during cooking, such as Maillard reaction products (Chaintreau, 2001). Kidney beans (250 g) were subjected to SDE (Nickerson & Likens, 1966) for 2 h using peroxide-free double-distilled diethyl ether (AR grade) as the extracting solvent. 2-Octanol (16.4 μ g; 200 μ L of 10^4 times diluted in methanol) was used as an internal standard. Ether extract was dried over anhydrous sodium sulfate and was then concentrated to a volume less than 5 mL using a Kuderna-Danish apparatus (Supelco) at 40 °C. The extract was then further concentrated to a volume of 50 μ L using a gentle stream of nitrogen; 1 μ L of concentrate was injected into the GC-MS (splitless mode).

2.2.3. Gas chromatography mass spectrometry (GC-MS) analysis

Analysis was carried out with a GC-MS instrument (QP5050 A; Shimadzu, Kyoto, Japan) equipped with an injection port having a special SPME glass liner (Supelco) and RTX-5 column (5% diphenyl dimethyl polysiloxane, 30 m \times 0.25 mm I.D.; Restek Corporation, Bellefonte, PA). The injection port was maintained at 270 °C for SPME samples whereas it was kept at 210 °C for SDE samples. There was no solvent delay for SPME samples whereas a 3-min delay was used for SDE samples. Helium was used as a carrier gas. GC column temperature was programmed as follows: 40 °C for 5 min and then increased to 200 °C at 4 °C min⁻¹, held for 5 min and then increased to 280 °C at 10 °C min⁻¹ with a final hold of 10 min. MS parameters were: ionisation voltage 70 eV, electron multiplier voltage, 1 kV and scan mode from *m/z* 35 to 350. The peaks were identified by comparing their mass fragmentation pattern and Kovats retention indices with those of standard compounds when available (Section 2.1) as well as from the data available in the spectral (Wiley/NIST) libraries of the instrument. Quantification was performed by comparing peak areas of compounds with that of the internal standard, and obtained as μ g kg⁻¹.

2.2.4. Sensory analysis

To prepare samples for sensory analysis, 20 g of beans were added into 120 mL of water and then subjected to autoclaving (120 °C, 15 psi, 15 min) in a 250-mL screw cap bottle (Schott Duran Group GmbH, Mainz, Germany). Aroma evaluation was done by quantitative descriptive analysis (QDA) as reported previously (Murray, Delahunty, & Baxter, 2001). The sensory panel consisted of 12 trained members, 7 males and 5 females. Five 60-min training sessions were carried out to generate attributes representative of the aroma of red kidney beans for descriptive analysis. After training sessions, five aroma attributes, i.e. 'smoky', 'sulfury', 'red kidney beans-like', 'earthy/raw potato' and 'boiled potato' were finalised for assessment. The intensity of each attribute was rated using an unstructured 14-cm line scale with extreme left as lowest value and extreme right representing the highest value for the assessed attribute. The samples labelled with random three-digit codes were presented in ventilated tasting booths illuminated with white light. All three varieties were assessed in triplicate by each panellist and sensory data were collected by measuring distance (cm) from origin. Sensory scores obtained were averaged and the results presented as a web diagram for all aroma attributes.

2.2.5. Statistical analysis

To visualise the differences in volatile aroma composition among all three varieties and further to observe changes in aroma

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