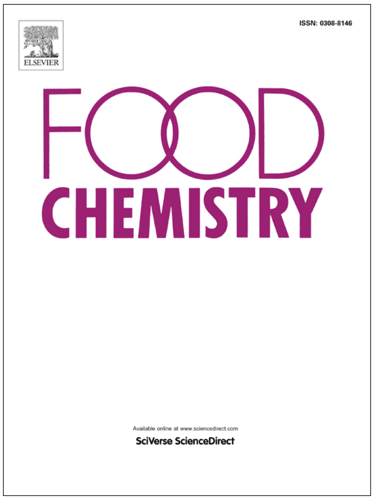

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Characterization of Typical Potent Odorants in Raw and Cooked *Toona sinensis* (A. Juss.) M. Roem. by Instrumental-Sensory Analysis Techniques

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ABSTRACT

Toona sinensis (A. Juss.) M. Roem. (TS) possesses a unique and pleasant flavor and is consumed as a popular seasonal vegetable in certain parts of eastern and southeastern Asia. The potent odorants in raw and cooked TS were identified by combined sensory and instrumental analysis techniques, including sensory descriptive aroma profiling and two complimentary volatile isolation methods combined with gas chromatography-olfactometry (GC-O) techniques. Highly volatile odorants were determined by static headspace dilution analysis (SHDA)-GC-O, while those of intermediate- and semi-volatility were determined by solvent-assisted flavor evaporation-aroma extract dilution analysis (SAFE-AEDA). Among the numerous odorants identified by SHDA and SAFE-AEDA, (*E*,*E*)-*bis*-(1-propenyl) disulfide was found to be predominant in both raw and cooked TS. In agreement with results of sensory descriptive analysis, hexanal, (*Z*)-3-hexenal, (*E*)-2-hexenal and (*Z*)-3-hexen-1-ol contributed green, grassy and leafy aroma notes; while hydrogen sulfide, methyl thiirane, (*E*,*E*)-*bis*-(1-propenyl) disulfide and (*E*,*Z*)-*bis*-(1-propenyl) disulfide contributed pungent, sulfurous and alliaceous notes in TS.

ARTICLE INFO

Keywords:

Toona sinensis, flavor, odorants, gas chromatography-olfactometry, gas chromatography-mass spectrometry, sensory descriptive analysis

1. Introduction

Toona sinensis (A. Juss.) M. Roem. (TS, also known as Xiangchun in Chinese or Chinese mahogany) is a member of family *Meliaceae*. It is a deciduous tree, and is cultivated in eastern and southeastern Asia, e.g., in North Korea, eastern, central and southwestern China, Nepal, northeastern India, Myanmar, Thailand, Malaysia and western Indonesia (Hsu, Huang, Chen, Mao, & Chaw, 2012). Because the young leaflets and tender shoots of TS have a pleasant aroma and are nutrient-dense, they have been consumed as vegetables. When the leaves are young, they are dark-red or red-brown and possess a strong and charactersitc aroma. However, when the leaves become older, they turn green, and their aroma intensity decreases. Raw TS shoots are seldom used directly as food materials, since they contain some toxic compounds (nitrites). After cooking (e.g. blanching), the leaves are served in salads, stir-fried with egg, pickled with salt, or roasted, dried and used as a healthy tea.

Recent studies on TS have mainly focused on the extraction and analysis of its nutrient substances, such as quercetin, gallic acid (Yu, Chang, Kuo, Tsai, & Chang, 2012), limonoids (Hu, Song, Mao, Wang, & Zhao, 2016) and flavonoid glycosides (Zhang et al., 2014).

Aroma is an important sensory attribute to TS. Nevertheless, there are very few reports on the volatile composition of TS. In these studies, nearly all of extraction methods used were based on headspace solid-phase microextraction (HS-SPME), and the columns used in gas chromatography-mass spectrometry (GC-MS) were nonpolar, such as HP-5, DB-5, or PE-5. Furthermore, the volatile substances were identified mainly by matching mass spectra with literature or databases. Only three previous studies have analyzed the aroma-active compounds in TS by gas chromatography-olfactometry (GC-O). Li and others analyzed the HS-SPME isolates of TS (from Beijing, China) by GC-O, and reported ten aroma-active regions, two of which were thought to possess the characteristic aroma of TS and believed to be sulfur-containing compounds based on GC/flame photometric detector (FPD) analysis. But, these two sulfur-containing compounds were not identified (Li, Wang, Dai, Su, & Chen, 2011). Liu et al. (2013) investigated the aroma-active compounds of TS (Shanxi, China) by SPME-GC-O. Twenty-six odorants were tentatively identified by their mass spectra and

GC retention indices (RI). Two compounds (*Z*)- and (*E*)- isomers of 2-mercapto-3,4-dimethyl-2,3-dihydrothiophene were thought to be major contributors to the characteristic aroma of TS, but their identities were not confirmed by analysis of authentic reference compounds (Liu et al., 2013). Using the same approach, Li et al. (2017) also studied the aroma-active compounds of TS (Tianjin, China). Fifteen aroma-active regions were detected, and 11 odorants were tentatively identified by only their mass spectra (Li, Wang, Zhao, & Liu, 2017). In the above studies, the compounds which contributed to the overall odor profiles of TS were not determined. In a separate study, (*S*,*S*)-*γ*-glutamyl-(*Z*-*S*-1-propenyl)thioglycine, (*S*,*S*)-*γ*-glutamyl-(*E*-*S*-1-propenyl)thioglycine and *γ*-glutamyl-(*Z*-*S*-1-propenyl)-cysteine were identified as potential nonvolatile precursors to volatile sulfur compounds in TS; however, the odor contribution of these volatile sulfur compounds were not determined (Li, Eidman, Gan, Haefliger, Carroll, & Pika, 2013).

A systematic and comprehensive study on the characteristic aroma-active components of TS is clearly warranted. Herein, we report on the combined use of various sensory- and instrumental-based analysis techniques to accomplish this task. The objectives of the present study were (1) to compare the sensory descriptive aroma profiles of raw and cooked TS; (2) to identify the aroma-active compounds in raw and cooked TS; (3) and to compare raw and cooked TS with respect to their predominant odorants.

2. Materials and Methods

2. 1. Samples

Three batches of fresh and tender TS shoots were purchased from a local supermarket (Yonghui Superstore, Beijing, China) in April and May 2017 (purchased within two weeks of each other). TS shoots were cultivated in Shandong Province, China. Sample preparation and preservation procedures were as follows: raw TS shoots were frozen by liquid nitrogen, then vacuum packaged in food grade polyethylene plastic storage bags and stored at -60 °C until analysis. Cooked TS shoots were blanched in boiling water (100 °C) for 60 s, cooled to room temperature, and then frozen and stored as described above.

2. 2. Chemicals

Authentic reference aroma compounds were supplied by the companies given in parentheses: acetaldehyde, ethanethiol, dimethyl sulfide, methyl thiirane, 2-methylpropanal, 3-methylbutanal, thiophene, 2,3-butanedione, methyl allyl sulfide, α-pinene, dimethyl disulfide, propyl sulfide, hexanal, 1-pentanethiol, 2-methyl-2-pentenal, 2,5-dimethylthiophene, α-terpinene, (*E*)-2-hexenal, butyl sulfide, 2-isopropyl-4-methylthiazole, 2,4,5-trimethylthiazole, (*E*,*E*)-2,4-hexadienal, methional, diallyl disulfide, (*Z*)-3-hexen-1-ol, linalool, (*E*,*Z*)-2,6-nonadien-1-al, β-caryophyllene, 3-methylbutanoic acid, 2-methyl-3-(methylthio)furan, borneol, 4-hydroxy-2,5-dimethyl-3(*2H*)-furanone and eugenol, mixture of (*Z*)-isoeugenol and (*E*)-isoeugenol, phenylacetic acid, vanillin and n-alkanes (C5−C28) (Sigma-Aldrich, St. Louis, MO); 2-methylbutanal, (*Z*)-3-hexenal and 1-octen-3-one (Bedoukian, Danbury, CT); (*Z*)-6-nonenal (Alfa Aesar, Lancashire, U.K.); allyl mercaptan (Fluka, Buchs, Switzerland); ethyl acetate (J.T. Baker Chemical Co, Phillipsburg, NJ); 1-hexanol (Polysciences Inc, Warrington, PA); and dimethyl trisulfide (Columbia Chemical Corporation Inc, Brunswick, Ohio).

Unless otherwise indicated, all reagent grade chemicals were obtained from Fisher Scientific (Fair Lawn, NJ), including anhydrous sodium sulfate (analytical grade), dichloromethane [high performance liquid chromatography (HPLC) grade] and sodium chloride (analytical grade). Anhydrous tetrahydrofuran (analytical grade) was purchased from Aladdin (Shanghai, China), sulfur powder (analytical grade, purified by precipitation) was obtained from Beijing Yili Fine Chemicals Co., Ltd (Beijing, China), magnesium chips, iodine beads (anhydrous) (*Z*)-1-bromo-1-propene (0.97) and (*E*)-1-bromo-1-propene (0.99) were purchased from Sigma-Aldrich and 1-propenylmagnesium bromide (0.5M solution in THF) was supplied by Acros Organics (United Kingdom).

Ultra-high-purity (UHP) nitrogen and UHP helium were purchased from S.J. Smith (Davenport, IA). Odorless distilled water was prepared by boiling glass-distilled water in an open flask until its volume was reduced by one-third of the original volume. Diethyl ether was freshly distilled prior to use.

2. 3. Synthesis of references

2. 3. 1. Synthesis of (Z or E)-1-propenylmagnesium bromide

A mixture of magnesium turnings (1.079 g, 450mmol), anhydrous tetrahydrofuran (40 mL) and iodine beads (0.091 g) was placed in a 100 mL three-neck flask fitted with a magnetic stir bar, an addition funnel, a condenser with drying tube and a rubber stopper for introducing N_2. A portion (1 mL) of a solution of (*Z*)-1-bromo-1-propene (0.97, 5 g, 41 mmol) or (*E*)-1-bromo-1-propene (0.99, 5 g, 41 mmol) in anhydrous tetrahydrofuran (10 mL) which was put into the addition funnel was added to the flask. The reaction mixture was heated by oil bath under stirring. The heating was not stopped until the color of iodine disappeared, and then the remaining 1-bromo-1-propene solution was added into the flask. Finally the flask was warmed for 30 min in oil bath at 80 °C to finish the preparation of the (*Z/E*)-1-propenylmagnesium bromide which was used for the next step.

2. 3. 2. Synthesis of bis-(1-propenyl) mono- and di-sulfides

The mixture from 2. 3. 1. was combined with sulfur powder (1.312 g, 41 mmol, in 40 mL anhydrous tetrahydrofuran) for synthesize bis-(1-propenyl) mono- and di-sulfides.

The same apparatus used in 2. 3. 1 was applied in this part, except that prior to the reaction the flask was cooled in an ice-water bath. 1-Propenylmagnesium bromide solution (30 mL, 15 mmol) was injected by syringe into the flask by piercing the rubber stopper. After addition of sulfur powder (544 mg, 20 mmol, in 20 mL anhydrous tetrahydrofuran) the reaction mixture was first stirred in ice bath for 0.5 h, and then for 0.5 h at room temperature. The reaction mixture was poured into a beaker containing a 30 g mixture of ice and water. The organic layer was separated, and the aqueous layer was extracted with diethyl ether (3 × 100 mL). The organic layer and the diethyl ether extracts were combined, washed with saturated sodium chloride solution (2 × 100 mL), dried over anhydrous sodium sulfate and then filtered to remove any debris. The filtrate was concentrated under a gentle stream of nitrogen gas. Characterization of *bis*-(1-propenyl) mono- and di-sulfides was carried out by GC-MS and GC-O-FPD.

(*Z*,*Z*)-*bis*-(1-propenyl) sulfide:

MS-EI m/z (%): 99 (100), 114 (95, M+), 45 (43), 39 (39), 85 (32), 41 (29), 71 (23), 72 (18), 73 (18), 59 (11); RI: 1200 (DB-WAX), 914 (HP-5MS).

(*E*,*Z*)-*bis*-(1-propenyl) sulfide:

MS-EI m/z (%): 99 (100), 114 (99, M+), 45 (44), 39 (38), 85 (32), 41 (29), 71 (23), 72 (19), 73 (18), 59 (12); RI: 1209 (DB-WAX), 923 (HP-5MS).

(*E*,*E*)-*bis*-(1-propenyl) sulfide:

MS-EI m/z (%): 114 (100, M+), 99 (97), 45 (44), 39 (35), 85 (33), 41 (29), 71 (23), 72 (18), 73 (18), 59 (12); RI: 1220 (DB-WAX), 926 (HP-5MS).

(*E*,*E*)-*bis*-(1-propenyl) disulfide:

MS-EI m/z (%): 146 (100, M+), 45 (92), 41 (60), 74 (58), 39 (55), 73 (46), 71 (34), 113 (34), 82 (24), 72 (10); RI: 1447 (DB-WAX), 1115 (HP-5MS).

(*E*,*Z*)-*bis*-(1-propenyl) disulfide:

MS-EI m/z (%): 45 (100), 146 (98, M+), 74 (72), 41 (71), 113 (60), 39 (58), 73 (40), 71 (38), 82 (22), 67 (20); RI: 1468 (DB-WAX), 1120 (HP-5MS).

(*Z*,*Z*)-*bis*-(1-propenyl) disulfide:

MS-EI m/z (%): 71 (100), 146 (75, M+), 45 (56), 113 (43), 41 (26), 39 (26), 73 (24), 82 (16), 74 (15), 72 (14); RI: 1491 (DB-WAX), 1126 (HP-5MS).

The relative proportions of isomers in the synthesis products were determined by GC-O-FPD.

From (Z)-1-bromo-1-propene

Bis-(1-propenyl) sulfide (*Z*,*Z*/*E*,*Z*/*E*,*E*): 77.7%/22.3%/0

Bis-(1-propenyl) disulfide (*Z,Z*/*E,Z*/*E,E*): 54.7%/23.6%/21.4%

From (E)-1-bromo-1-propene

Bis-(1-propenyl) sulfide (*Z,Z*/*E,Z*/*E,E*): 0/21.4%/78.6%

Bis-(1-propenyl) disulfide (*Z,Z*/*E,Z*/*E,E*): 0/0/100%

From 1-propenylmagnesium bromide (Z and E mixture)

Bis-(1-propenyl) sulfide (*Z,Z*/*E,Z*/*E,E*): 25.3%/42.2%/32.5%

Bis-(1-propenyl) disulfide (*Z,Z*/*E,Z*/*E,E*): 54.5%/25.7%/19.8%

2. 4. Sensory Aroma Profiling

Aroma profiles were determined following closely the method previously descibed by Zhou, Wintersteen, & Cadwallader (2002). Panelists (4 male and 7 female, consisting of university students/staff, 23−48 years of age) had previously received extensive training in descriptive sensory analysis (>20 h), specifically in flavor profiling of various food samples. The panel underwent an additional 4 h of training to become familiar with the evaluation of TS aroma. Raw or cooked TS (chopped, 3.5 g) was placed in a 500 mL low density polyethylene (LDPE) wash bottle with siphon tubes removed from the caps. Bottles were covered with aluminum foil to minimize visual bias and labeled with random 3 digit codes. Samples were equilibrated at room temperature (approx. 27 °C) for 30 min before presenting to panelists. Panelists evaluated each sample by gently squeezing the bottle and taking short sniffs of the air emitted from the nozzle. Aroma intensities were scored on 15 cm universal scales anchored on the left with “none” and on the right with “very strong” which corresponded to intensity ratings of 0 and 15, respectively (Meilgaard, Civille, & Carr, 1999). Each term was anchored with a standard reference with an intensity rating determined by the panel, as follows: “green/grassy” represented by 1.0 g of cut-grass (intensity score of 12); “cooked meat” represented by 0.2 g of a ground vitamin B pill (intensity score of 10); “alliaceous” represented by 0.9 g of chopped raw garlic (intensity score of 14); “earthy” represented by 3.2 g of chopped Hershey’s dark chocolate (intensity score of 9); “pungent” represented by 1.4 g of chopped raw onion (intensity score of 13). Individual panelist rating results were revealed at the end of each sensory analysis session, and final aroma profiles of the samples were reported on the basis of discussion and by consensus of the panel.

2. 5. Isolation of Volatile Compounds.

2. 5. 1. Static Headspace

The procedure was based on the method described by Cadwallader, Potts, Brisske-BeVier, & Mirarefi (2011) with some modifications. Chopped TS (5 g) was placed in a 60 mL glass serum vial. The vial was sealed with a polytetrafluoroethylene (PTFE) faced silicon septum and then incubated in a water bath at 35 °C for 25 minutes. Following incubation, a headspace volume was withdrawn for GC-O. A fresh sample was used for each headspace volume tested.

2. 5. 2. Direct Solvent Extraction and Solvent-Assisted Flavor Evaporation (DSE-SAFE)

Thirty grams of raw or cooked TS chopped shoots plus 30 g of sodium chloride were added to in a 250 mL glass bottle. The bottle was frozen (-60 °C) and then dichloromethane (120 mL, at -60 °C), avoiding to produce thermal artifacts during homogenizing, was added, and the mixture homogenized by Ultra Turrax (IKE, Germany) at the speed of 10000 rpm for 2 min. The blended sample was passed through a Whatman No. 4 filter paper and the filter cake was washed twice with 10 mL of dichloromethane.

The solvent extract was subjected to SAFE in order to remove any nonvolatile material. SAFE (ACE Glassware, Vineland, NJ) was conducted for for 2.5 h at 40 °C as described previously (Rotsatchakul, Chaiseri, & Cadwallader, 2008). The resulting aroma extract was concentrated to 5 mL using a 15 cm Vigreux column at 45 °C water bath. Final extract was dried over 1 g of anhydrous sodium sulfate and then further concentrated under a gentle stream of nitrogen to 400 μL. Extracts were transferred to 2 mL amber glass vials equipped with PTFE-lined closures and stored at -60 °C until analysis.

2. 5. 3. HS-SPME

HS-SPME-GC-MS was used to aid in the identification of odorants detected by static headspace and SAFE. A 2-cm SPME fiber, coated with 50/30 μm divinylbenzene/carboxen/polydimethyl siloxane (Supelco, Bellefonte, PA, U.S.) was preconditioned at 270 °C for 1 h prior to analysis. For analysis, a sample (8 g, chopped raw or cooked TS) was transferred to a 40 mL static headspace amber glass bottle and the bottle sealed with an aluminum cap (with PTFE /silicon septum, thickness 1.3 mm; Supelco). The operating conditions for HS-SPME were as follows: pre-incubation and absorption temperature, 35 °C; pre-incubation time, 20 min; absorption time, 20 min; GC desorption time, 10 min; GC desorption temperature, 250 °C. Analyses were performed in duplicate.

2. 6. Analysis of Volatile Compounds

2. 6. 1. GC-O Conditions for Static Headspace Dilution Analysis (SHDA)

SHDA was performed using an Agilent 6890N GC (Agilent Technologies, Inc.; Palo Alto, CA, U.S.) equipped with an flame ionization detector (FID) and olfactory detector port (ODP2, Gerstel). Separations were preformed using either an RTX-WAX (15 m × 0.53 mm × 1.0 μm; Restek, Bellefonte, PA) or RXI-5MS (15 m × 0.53 mm × 0.5 μm; Restek) GC column. Following incubation, a headspace volume (25, 5, 1, 0.2 or 0.04 mL) was withdrawn by means of a heated (45 °C) gas-tight syringe which injected the same volume of headspace they would withdraw from glass vials, then withdraw the headspace as follows: 25 mL syringe for 25 mL headspace, 5 mL syringe for 5 mL headspace, 1 mL syringe for 1 mL headspace, 250 μL syringe for 200 μL headspace, 50 μL syringe for 40 μL headspace, and 10 μL syringe for 5 μL headspace. Then the syringe injected into a CIS-4 cooled injection system (Gerstel GmbH & Co. KG, Germany) operating in the solvent vent mode (vent pressure, 8.5 psi; vent flow, 25.0 mL/min; splitless time, 1.5 min); initial temperature, -120 °C (0.1 min hold); ramp rate at 12 °C/s to 220 °C (10 min hold); to final temperature at the same ramp rate, 260 °C (10 min hold).Column effluent was split (1:5) between FID and ODP using two deactivated fused silica capillaries. FID and olfactory transfer line temperatures were set to 250 °C. The GC oven temperature was programmed from 35 °C (hold for 5 min) to 225 °C (hold for 30 min) at a rate of 6 °C/min (for both RTX-WAX and RXI-5MS columns). The carrier gas was helium at a constant flow rate of 5 mL/min. The makeup gases of the ODP consisted of nitrogen (sheath gas) and humidified air (nose cone). Odor qualities (by GC-O) were determined by three panelists (1 female and 2 males, 24−54 years old). The details of the procedure have been previously described (Lapsongphon, Yongsawatdigul, & Cadwallader, 2015; Zhou et al., 2002).

2. 6. 2. GC-O Conditions for Aroma Extract Dilution Analysis (AEDA)

Each aroma extract from DSE-SAFE was stepwise diluted (1:3,v/v) with dichloromethane according to the general AEDA technique (Grosch, 1994). The diluted samples were transfered to PTFE-lined screw caps and stored at -60 °C prior to analysis. GC-O was conducted using a 6890N GC (Agilent Technologies Inc.) equipped with a FID and an ODP2. The aroma extract (2 μL) was injected in the cool on-column mode (+3 °C oven tracking mode) to avoid injection bias and reduce the chance for thermal degradation of any labile compounds. The conditions for GC analysis were the same as those used for GC-O in 2. 6. 1, except the ramp rate was 10 °C/min for the RTX-WAX column and 6 °C/min for the RTX-5MS column. GC-O was conducted by four panelists (2 female and 2 males, 20−32 years old).

2. 6. 3. GC-O Conditions for SPME

GC-O for SPME was carried out using an Agilent 7890 GC equipped with a FID or a FPD (Agilent Technologies Inc.) and an ODP (ODP3, Gerstel). The effluent was split between the FID/FPD and ODP in a 1:2 ratio by volume using Y-type splitter and two deactivated fused silica capillaries. The FID and FPD were held at 250 °C and 200 °C, respectively. The temperature of the ODP transfer line was 200 °C. SPME samples were analyzed using a DB-WAX column (30 m × 250 μm × 0.25 μm; Agilent Technologies Inc.) or an HP-5MS column (30 m × 0.25 mm × 0.25 μm; Agilent Technologies Inc.). Initial oven temperature was 35 °C (held for 5 min), then increased to 225 °C at 10 °C/min (DB-WAX) or 6 °C/min (HP-5MS), with a final hold time of 30 min. Injection was done in the hot splitless mode (4 min valve-delay) at 250 °C (for FID) or 150 °C (for FPD). Helium was used as the carrier gas at a constant flow rate of 1 mL/min. The effluent sent to the ODP was combined with a stream of humidified air.

2. 6. 4. GC-MS

Analyses were conducted using an Agilent 7890B GC coupled to a 5977A mass-selective detector (MSD) (Agilent Technologies Inc.). The SAFE isolates (2 μL) or SPME extracts were analyzed on both a DB-WAX capillary column (30 m × 0.25 mm × 0.25 μm; Agilent Technologies Inc.) and an HP-5MS column (30 m × 0.25 mm × 0.25 μm; Agilent Technologies Inc..). Initial oven temperature was 35 °C (held for 5 min), then increased to 225 °C at 10 °C/min (DB-WAX) or 6 °C/min (HP-5MS), with a final hold time of 30 min.. Injections were made in the hot splitless mode (250 °C; 4 min valve-delay). The carrier gas was helium at a constant flow rate of 1 mL/min.. The MSD conditions were as follows: capillary direct interface temperature, 250 °C; mass quadrupole temperature, 150 °C; ionization energy, 70 eV; ion source temperature, 230 °C; mass range, 33–300 amu; EM voltage, autotune, +200 V; scan rate, 5.3 sans/s. The chromatograms were analyzed using MassHunter Qualitative Analysis Software B.06.00 (Agilent Technologies, Inc.).

2. 7. Compound Identification

The retention index (RI) of each compound was calculated using the retention time (RT) of that compound compared against the RTs of a series of standard n-alkanes (C5-18 for non-polar column: RXI-5MS and HP-5MS, C5-28 for polar columns: RTX-WAX and DB-WAX), according to Van Den Dool, & Kratz (1963). The RI values, in combination with aroma descriptions, FPD and mass spectral library results (2014 National Institute of Standards and Technology), were compared with literature values and online databases (Flavornet and NIST Chemistry WebBook) to provide tentative compound identifications. Authentic standards of tentatively identified compounds were analyzed by GC-O and GC-MS to confirm their RIs and aroma attributes for the purpose of positive identification.

3. Results and discussion

3. 1. Sensory Aroma Profiles of Raw and Cooked TS

To obtain an idea of the overall aroma profiles of raw and cooked TS, sensory descriptive analysis was performed by rating six main aroma attributes including alliaceous, cooked meat, earthy, green/grassy, pungent and overall intensity (Figure 1). Except for the green/grassy note, the intensities of the all aroma attributes were higher in cooked TS than in raw TS. In contrast the green/grassy attribute had the strongest intensity in raw TS, followed by pungent, alliaceous, cooked meat and earthy notes. In cooked TS, the alliaceous attribute had the strongest intensity, followed by pungent, green/grassy, cooked meat and earthy notes. The following sections describe the results of sensory-instrumental based methods for the identification of the potent odorants responsible for the characteristic aroma of raw and cooked TS.

3. 2. Potent Headspace Odorants Detected by SHDA

In the case when aroma isolation is done by extraction techiques, some highly volatile compounds might be overlooked because they can be lost during the various preparation and workup steps employed. For this reason the highly volatile aroma compounds were evaluated in this study by the SHDA. Prior to the analysis, the static headspace above TS was collected using a gas-tight syringe, then expelled out toward to the noses of panelists to make sure the captured headspace possessed the characteristic odor expected for TS. Similar odors descriptions were used by panelists to describe the odors compared with those for the sensory aroma profiles for TS. Based on these results, SHDA was thought to be a good way to analysize high volatile aroma compounds in TS, and the most potent compounds could be screened by analysis of decreasing static headspace volumes.

A total of 32 and 36 aroma-active regions were detected in the the static headspace of raw and cooked TS, respectively, on both RTX-5MS and RTX-WAX columns (Table 1). Twenty-five odorants were common constituents of raw and cooked TS. Most of the compounds identified in TS (nos. 1, 2, 4, 5, 10, 11, 13, 19, 20, 22, 26, 29, 32, 33, 37, 41, 42, 45, 47-49, 65, 71 and 75) were sulfur-containing compounds. The results of SHDA also supported the differences between raw and cooked TS as indicated by the sensory aroma profiles. For example, aldehydes and alchohol containing six carbons (nos. 21, 24, 30 and 50) contributed green, grassy and leafy notes. Certain sulfur compounds (nos. 32, 33, 37, 42, 46 and 48) contributed cooked meat notes, while some other sulfur-containing odorants and two unknown compounds (nos. 9, 10, 11, 13, 26 and 51) contributed alliaceous notes. These compounds were detected at higher flavor dilution (FD) factors in cooked TS than in raw TS. This is in agreement with the sensory results which showed that cooked TS had higher intensities for cooked meat and alliaceous notes. Some aldehydes and sulfur compounds (nos. 1, 3, 4, 5 and 7) were described as pungent, and some other compounds, including aldehydes and terpenes (nos. 12, 18, 27 and 61) contributed earthy notes.

Among the compounds identified in raw TS, acetaldehyde, dimethyl sulfide, 2-/3-methylbutanal, (*Z*)-3-hexenal, α-terpinene and (*E,E*)-*bis*-(1-propenyl) disulfide were detected at a relatively high FD factor of 25, followed by 2-methylpropanal, allyl mercaptan, methyl thiirane, 2,3-butanedione, hexanal, diisopropyl disulfide and (*Z*)-3-hexen-1-ol detected, all of which had an FD factor of 5.

Among the odorants identified in cooked TS, hydrogen sulfide had the highest FD factor of 625, followed by dimethyl sulfide, methyl thiirane, hexanal, (Z)-3-hexenal, 2,5-dimethylthiophene, dibutyl sulfide, 2-isopropyl-4-methylthiazole, dimethyl trisulfide, (*E,E*)-*bis*-(1-propenyl) disulfide, linalool and β-caryophyllene with FD factors of 25. Acetaldehyde, ethanethiol, thiophene, α-pinene, α-terpinene and (*E,E*)-*bis*-(1-propenyl) disulfide were detected at an FD factor of 5.

With respect to odorants found in both raw and cooked TS, some compounds (nos. 3, 7, 10, 12, 15, 27, 32, 50) which had high FD factors (≥ 5) in raw TS had lower FD factors in cooked TS, except for dimethyl sulfide, (*Z*)-3-hexenal and (*E,E*)-*bis*-(1-propenyl) disulfide which had the same FD factor in both raw and cooked TS. Some compounds (nos. 2, 12, 30, 32, 35, 50, 59) were only detected in raw TS. There were two possible reasons for this. The first was that these compounds might react with other compounds to form new substances during blanching. The second was that they possibly leached into the water during blanching so that these odorants had lower FD factors or couldn’t be detected in cooked TS. However, some compounds (nos. 11, 18, 21, 33, 37, 42, 48 and 61) had higher FD factors in cooked TS than in raw TS. Additionally, some odorants (nos. 1, 4, 9, 13, 26, 40, 51, 55, 66, 75 and 87) were only detected in cooked TS.

3. 3. Potent Odorants Detected by AEDA

A total of 59 odorants were detected in TS by AEDA (Table 2). Results of AEDA were in good general agreement with those of SHDA, with 29 of the compounds detected by AEDA also found by SHDA. Seven highly volatile compounds (nos. 1, 2, 3, 5, 7, 9 and 10) detected by SHDA were not detected by AEDA. In contrast, 12 odorants with intermediate and low volatilities (nos. 74, 76-86 and 88) were only detected by AEDA. Odorants identified by AEDA included those with green, grassy and leafy (nos.21, 24, 25, 30, 40 and 50), cooked meat (nos. 28, 29, 32, 33, 37, 41, 42, 47, 48 and 65), alliaceous (garlic-like, cooked onion-like) (nos. 8, 11, 19, 49 and 81), pungent (nos. 4, 22 and 80), earthy (nos. 12, 18, 27, 58, 61 and 78) and sweet notes (nos. 66, 72, 79, 82, 83, 85-88).

Fifty-five odorants were detected in raw TS, with (*E*,*E*)-*bis*-(1-propenyl) disulfide having the highest FD factor of 19683, followed by an unknown compound (no. 58; woody, pine), *β*-caryophyllene, (*Z*)-isoeugenol, phenylacetic acid and vanillin detected at an FD of 729. Hexanal, (*Z*)-3-hexenal, methional, linalool, unknown (no. 80; pungent, sweaty) and cinnamyl acetate were all detected at a somewhat lower FD factor of 243. An additional 5 odorants, all with FD factors of 81, were identified as 2-methyl-2-pentenal, 2,4,5-trimethylthiazole, 3-methylbutanoic acid, geraniol and eugenol.

Forty-eight odorants were detected in cooked TS. (*E*,*E*)-*Bis*-(1-propenyl) disulfide had the highest FD factor of 59049, followed by (*E*,*Z*)-*bis*-(1-propenyl) disulfide (FD factor of 6561) and 2,4-dimethylthiophene, 2,4,5-trimethylthiazole, *β*-caryophyllene, borneol, (*Z*)-isoeugenol, phenylacetic acid and vanillin (All with an FD factor of 2187). Odorants having an FD factor of 729 were identified as methyl thiirane, (*Z*)-3-hexen-1-ol, unknown (no. 72; sweet, woody, fruity, mint), cinnamyl acetate and *p*-vinyl guaiacol. An FD factor of 243 was assigned to dimethyl disulfide, (*E*)-4,5-expoxy-(*E*)-2-decenal and eugenol.

Forty-four volatile compounds were commonly detected in raw and cooked TS. Those with relatively high FD factors were (*E*,*E*)-*bis*-(1-propenyl) disulfide, *β*-caryophyllene, (*Z*)-isoeugenol, phenylacetic acid, vanillin and cinnamyl acetate. Hexanal, (*Z*)-3-hexenal, two unknowns (no. 58; woody, pine; and no. 80; pungent, sweaty) and linalool had higher FD factors in raw than in cooked TS, as blanching in boiling water might decrease the contents of these compounds. This could explain why people blanch TS to remove green and grassy notes. Compared with raw TS, sulfur compounds had much higher FD-factors in cooked TS and contributed cooked meat and alliaceous notes. These included methyl thiirane, dimethyl disulfide, 2,5-dimethylthiophene, *bis*-(1-propenyl) sulfide, isopropyl disulfide, 2,4,5-trimethylthiazole, (*E*,*E*)-*bis*-(1-propenyl) disulfide and (*E*,*Z*)-*bis*-(1-propenyl) disulfide. In addition, compounds with high FD factors in cooked TS that contributed sweet and woody odor characteristics were *β*-caryophyllene, borneol, (*E*)-4,5-expoxy-(*E*)-2-decenal, cinnamyl acetate, eugenol, *p*-vinyl guaiacol, (*Z*)-isoeugenol, (*E*)-isoeugenol, phenylacetic acid and vanillin.

3. 4. Aroma Chemistry of TS

The green/grassy attribute was predominant in the aroma profile of raw TS (Figure 1); whereas, cooked TS possessed high intensities of alliaceous and pungent notes. Based on the results of SHDA and AEDA, several sulfur-containing compounds were identified as potent odorants in TS, and they contributed cooked meat, alliaceous and pungent notes. In addition, phenolic compounds imparted sweet notes in TS, especially in cooked TS.

3.4.1 Potent Sulfur-Containing Odorants in TS

A total of 51 odorants were detected by SPME in the static headspace of TS (Table 3). Twenty-two of volatile compounds detected in SPME extracts were also found in static headspace and SAFE isolates. In agreement with the results of SHDA, hydrogen sulfide, acetaldehyde, 2-methylpropanal, allyl mercaptan, 2,5-dimethylthiophene, an unknown (no. 51; sulfurous, alliaceous) and (*E*,*E*)-*bis*-1-(1-propenyl) trisulfide were also detected in SPME extracts. Whereas, 2,4-dimethylthiophene, 2-

isobutyl-3-methoxypyrazine, α-farnesene, eugenol, (*Z*)-isoeugenol and (*E*)-isoeugenol were detected in both SPME extracts and SAFE isolates. Therefore, results of SPME were in good general agreement with the SHDA and SAFE results, since SPME mainly measured volatiles with high and intermediate volatility; however, some odorants with low volatilities were also detected.

Sixteen odorants were detected only by the SPME. The included 10 sulfur-containing compounds. Noteworthy among these were 3,4-dimethylthiophene, (*Z*)-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene and (*E*)-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene. Liu et al (2013) had previously reported the above four compounds in TS by SPME-GC analysis.

In the present study (*E,E*)-*bis*-(1-propenyl) disulfide, (*E,Z*)-*bis*-(1-propenyl) disulfide and (*Z,Z*)-*bis*-(1-propenyl) disulfide were positively identified by their RIs, odor descriptions, mass spectra and by comparison with synthesized standard compounds. They were further comfirmed by GC-FPD analysis (by both SAFE and SPME). Previously, the *bis*-(1-propenyl) disulfides were only tentatively identified in TS seedlings and tender shoots by comparison of their mass spectra to those published in a mass spectral library database (Li et al, 2017).

The *bis*-(1-propenyl) disulfides (nos. 46-48), which are common components of Allium distilled oils, have been reported to rearrange at 85 °C into 2-mercapto-3,4-dimethyl-2,3-dihydrothiophene, which could then futher degraded to form 3,4-dimethylthiophene or 3,4-dimethyl-2-thienyl disulfides (Figure 2; Block, Bayer, Naganathan, & Zhao, 1996). These researchers found that significant qualities of 2-mercapto-3,4-dimethyl-2,3-dihydrothiophene and 3,4-dimethylthiophene were formed when GC injector temperatures of 250-280 °C were used, but were not detected when a lower injector temperature of 120 °C was used (Block, Putman, & Zhao, 1992). In the above reaction, a dithio-Claisen rearrangement was proposed as the key step (Block, & Shu, 1990). Elsewhere, 2,4-dimethylthiophene, 3,4-dimethylthiophene (no. 31), 2,5-dimethylthiophene, (*Z*)-mercapto-3,4-dimethyl-2,3-dihydrothiophene (no. 63) and (*E*)-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene (no. 67) were identified in distilled oils of Welsh onions and scallions (Kuo, & Ho, 1992).

We performed additional experiments to better understand the effect of GC injection port temperature on the stability and formation of sulfur-containing compounds found in TS. For this comparison the temperature of MSD transfer line was held constant at 200 °C. It was found that the abundance of compounds nos. 31, 63 and 67 increased significantly as a function of increasing injection port temperature from 175 °C to 250 °C (Table 4); whereas, compounds nos. 46, 47 and 48 all decreased. At all injection temperatures, (*E,E*)-*bis*-(1-propenyl) disulfide and (*E*,*Z*)-*bis*-(1-propenyl) were always detected at higher abundance than (*Z,Z*)-*bis*-(1-propenyl) disulfide. Furthermore, (*Z,Z*)-*bis*-(1-propenyl) disulfide was not detected when an inlet temperature above 225 °C was used.

These above three compounds (nos. 31, 63 and 67) could be detected when inlet injector temperature was 175 °C, which meant that the *bis*-(1-propenyl) disulfides (nos. 46-48) had degraded. When an inlet temperature at 150 °C was applied for GC-O/FPD (SAFE and SPME), peaks for these compounds (nos. 31, 63 and 67) were still detected in raw and cooked TS, and the corresponding odors could be recognized by GC-O.

That fact that the disulfides in TS are thermally labile makes procedures that rely on thermal desorption, such as SPME which requires hot split/splitless injection, unrealiable. A better alterntative to avoid thermal decomposition of the disulfides would be to use technique that utilizes low temperature injection, such as the analysis of aroma extracts by cool on-column injection or static headspace analysis using cyrogenic solvent-vent mode injection. This explains why compounds nos. 31, 63 and 67 were not detected by SHDA and AEDA, while instead *bis*-(1-propenyl) disulfides (nos. 46-48) were identified with the highest FD-factors in raw and cooked TS. Therefore, results of SHDA and AEDA better represent the true aroma profiles of raw and cooked TS.

Volatile sulfur compounds clearly made the greatest contribution to the characteristic aroma of TS. In particular, (*E*,*E*)-*bis*-(1-propenyl) disulfide, (*E*,*Z*)-*bis*-(1-propenyl) disulfide and (*Z*,*Z*)-*bis*-(1-propenyl) disulfide appear to make the greatest contribution to the overall aroma profile of TS, especially cooked TS. *Bis*-(1-propenyl) sulfides and (*E*,*E*)-*bis*-(1-propenyl) trisulfide were also identified with low FD factors. The nonvolatile precursors for these compounds were previously identified as (*S*,*S*)-*γ*-glutamyl-(*Z*-*S*-1-propenyl)thioglycine, (*S*,*S*)-*γ*-glutamyl-(*E*-*S*-1-propenyl)-thioglycine, *γ*-glutamyl-(*Z*-*S*-1-propenyl)-cysteine, γ-glutamyl-(*E*-*S*-1-propenyl)-cysteine, *Z*-*S*-1-propenyl-*L*-cycsteine and *E*-*S*-1-propenyl-*L*-cycsteine (Li et al., 2013). Hydrogen sulfide formed by Strecker degradation from cysteine, was detected in cooked TS at a high FD factor by SHDA Hydrogen sulfide is highly volatile compound that can easily be recognized even at trace concentrations, which might be the one reason why cooked TS has an unique odor after cooking. Allyl mercaptan and methyl thiirane were identified in raw and cooked TS, and methyl thiirane had a higher FD-factor in cooked TS as it could be formed during blanching. The (*Z*)- and (*E*)-1-propenyl mercaptans are isomers of allyl mercaptan and methyl thiirane, but they weren’t detected in raw and cooked TS. These two compounds are believed to be very unstable precursors of methyl thiirane and *bis*-(1-propenyl) sulfides (Li et al., 2013).

During the Strecker degradation, 2-methylbutanal, 3-methylbutanal and methional can be formed from leucine, isoleucine and methionine, respectively (Parker, 2014). Methional can undergo subsequent degradation to acrolein and methanthiol. Methanthiol easily oxidises to form dimethyl disulfide (Granvogl, Beksan, & Schieberle, 2012). Dimethyl sulfide can also be formed from a thermal degradation of *S*-methylmethionine (vitamin U), which is the *S*-methylated form of methionine and a non-proteinogenic amino acid that occurs in various vegetables (Scherb, Kreissl, Haupt, & Schieberle, 2009). Methional and dimethyl sulfide were also identified in tomato paste (Buttery, Teranishi, Ling, & Turnbaugh, 1990) and cooked asparagus (Ulrich, Hoberg, Bittner, Engewald, & Meilchen, 2001).

In general, thiazoles are mainly formed by non-enzymatic browning reactions between reducing sugars and amino acids in the presence of hydrogen sulfide. 2,4,5-Trimethylthiazole was detected in TS and contributed a sulfurous, vegetable odor note to overall aroma profile. This compound can be generated form the reaction between ascorbic acid and cysteine (Yu, & Zhang, 2010).

3.4.2 Potent Green, Grassy and Leafy Smelling Compounds in TS

Several C6-aldehydes and C6-alcohols contributed green, grassy, and leafy aroma notes to TS, especially to raw TS. These included hexanal (grassy, leafy), (*Z*)-3-hexenal (grassy, leafy), (*E*)-2-hexenal (green, leafy), 1-hexanol (green) and (*Z*)-3-hexen-1-ol (green, leafy). These volatile compounds are synthesized in green leaves from α-linolenic and linoleic acids bia biosynthetic pathways (lipoxygenase and hydroperoxide lyase) (Hatanaka, 1993). The metabolism of polyunsaturated fatty acids through the lipoxygenase pathway is known to generate of the "green" aroma notes in many vegetables and fruits (Raffo, Masci, Moneta, Nicoli, Pulgar, & Paoletti, 2018).

3.4.3 Potent Sweet Compounds in TS

Several phenolic compounds with herbal, sweet, cloves and vanilla-like aroma notes were identified as potent odorants in TS. These included cinnamyl acetate (sweet, spicy), eugenol (sweet, woody, cloves), *p*-vinylguaiacol (sweet, woody, cloves), (*Z*)- and (*E*)-isoeugenol (sweet, spicy, cloves), phenylacetic acid (floral, rose) and vanillin (sweet, caramel). These compounds had high FD factors in both raw and cooked TS. None of these compounds have been previously identified in TS, especially in cooked TS. Some of these compounds might originate from degradation of ferulic acid (Fiddler, Parker, Wasserman, & Doerr, 2002). Phenylacetic acid was possibly formed via the Strecker degradation of phenylalanine (Hofmann, Münch, & Schieberle, 2000). Previously, some phenolic antioxidants were identified in TS (fresh young leaves and shoots), including gallic acid and its derivatives, gallotannins and flavonoids (Wang, Yang, & Zhang, 2007; Yang, Wang, Xing, Dai, & Chen, 2011). However, the odorants with sweet notes and high FD-factors couldn't be perceived during sensory aroma analysis. It could be these compounds have high boiling points, such as, cinnamyl acetate (265 °C), eugenol (254 °C), p-vinylguaiacol (224 °C), isoeugenol (266 °C), phenylacetic acid (265.5 °C) and vanillin (285 °C), or they are at low concentrations such that their odors could be suppressed by other high abundance volatile compounds.

Linalool (floral, sweet, lemon) had high odor potency in raw TS. This odorant is reported as one of the most aroma-active compounds contributing to the overall flavor of orange peel oil (Dharmawan, Kasapis, Sriramula, Lear, & Curran, 2009; Fischer, & Schieberle, 2009). It is also a major component of the beverage prepared from Darjeeling black tea (Schuh, & Schieberle, 2006). β-Caryophyllene (sweet, woody) had high FD factors in raw TS (FD = 729) and cooked TS (FD = 2187), and this compound was also identified in TS by microwave-assisted extraction-(MAE)-HS-SPME followed by GC–MS and was in highest abundance among 45 compounds reported (Mu, Wang, Liu, Yuan,Wang, & Fan, 2007).

4. Conclusions

The study represents the first comprehensive determination of the potent aroma components of raw and cooked TS, and clearly demonstrates the importance of sulfur-containing odorants, especially, (*E,E*)-*bis*-(1-propenyl) disulfide and (*E,Z*)-*bis*-(1-propenyl) disulfide, in the overall aroma of cooked TS. These and other sulfur-containing compounds contribute cooked meat, alliaceous and pungent aroma notes, while other compounds provide green/grassy, woody and sweet aroma notes. Collectively, these potent odorants produce the unique and characteristic aroma profile of TS.

Additional studies should be considered, including quantitative analysis and determinination of odor-activity values of potent odorants along with aroma recombination studies. Meanwhile, the thermal degradation for some sulfur compounds in TS should be further investigated during cooking as well as during the aroma isolation procedures and instrumental analyses.

Conflict of interest statement

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at

Figures showing standard mass spectras for (Z,Z)/(E,Z)/(E,E)-bis (1-propenyl) disulfide isomers (Figure S1), mass spectras comparision between samples' and standard databases' in NIST 14 (Figure S2); table containing data for all compounds listed in Table 1, 2, 3 and 4 (Table S1).

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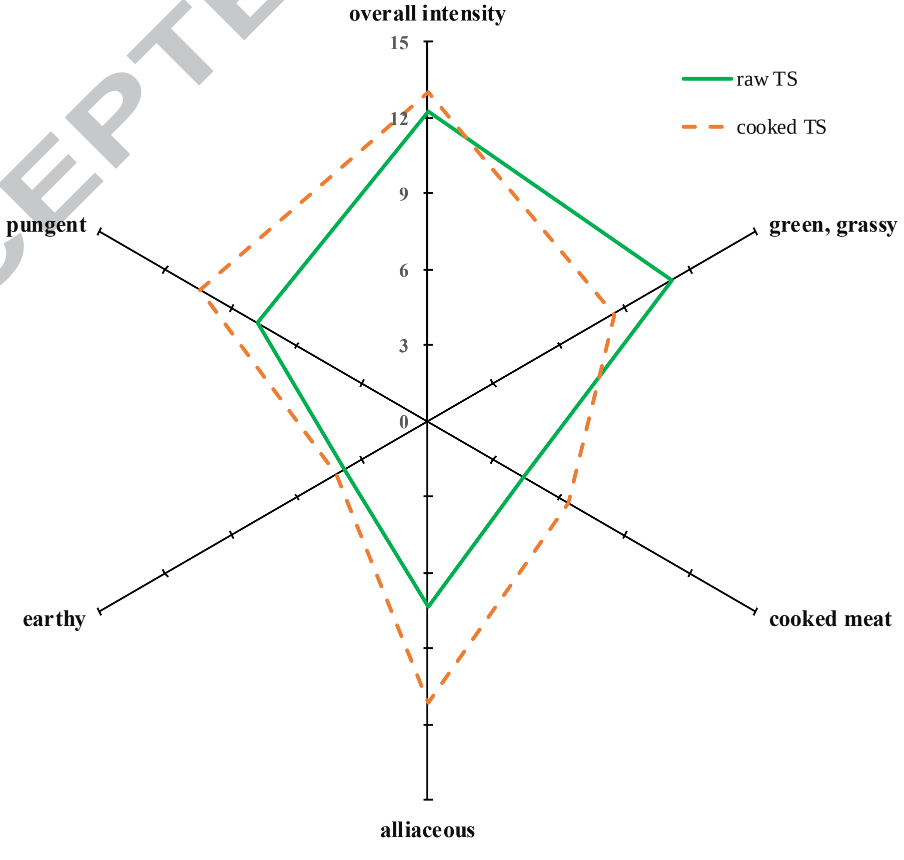
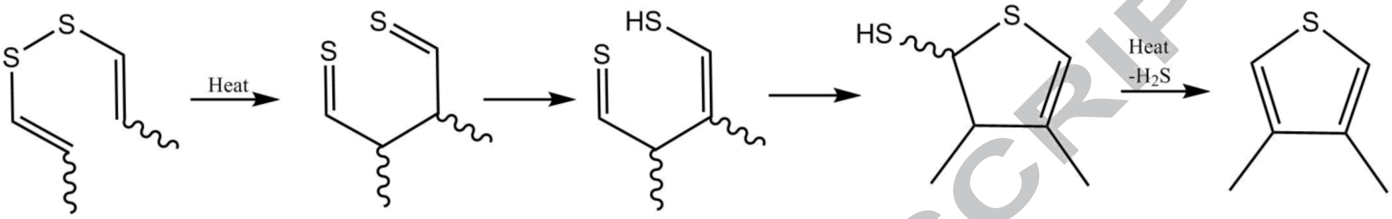


Figure 1. Sensory aroma profile comparison of raw and cooked *Toona sinensis.* [Intensity from 0 to 15, where 0 = none, 15 = very strong.]



nos. 46-48

nos. 63, 67

no.31

Figure 2. Thermal degradation of bis-(1-propenyl) disulfides (nos. 46-48) to form compounds nos. 31, 63 and 67.

Table 1. Odorants Detected by GCO-Static Headspace Dilution Analysis of *Toona sinensis*

no. [a]	*retention index* [b]		*compound*	*odor description* [c]	*FD-factor* [d]			
					raw Toona sinensis		*cooked Toona sinensis*	
	RTX-WAX	*RXI-5MS*			*RTX-WAX*	*RXI-5MS*	*RTX-WAX*	*RXI-5MS*
1	<500	<500	hydrogen sulfide [f]	rotten egg			625	125
5	752	517	dimethyl sulfide [i]	pungent, sweet, corn	25	25	25	25
46	1450	1108	(*E*,*E*)-*bis*-(1-propenyl) disulfide [h]	sulfurous, cooked onion	25	25	25	25
11	916	587	methyl thiirane [i]	alliaceous, pungent, garlic	5	1	25	25
37	1343	1017	2-isopropyl-4-methylthiazole [i]	sulfurous	1	1	25	25
42	1376	986	dimethyl trisulfide [i]	sulfurous, cooked cabbage	1	1	25	25
26	1158	869	2,5-dimethylthiophene [i]	sulfurous, garlic			25	1
33	1263		dibutyl sulfide [i]	sulfurous, green	1		25	
61	1586		β-caryophyllene [i]	sweet, woody	1		25	
9	854		unknown	alliaceous, garlic			25	
51	1490		unknown	sulfurous, alliaceous			25	
55	1532		linalool [i]	floral, sweet, lemon			25	
3	617	<500	acetaldehyde [i]	pungent, yogurt	5	25	5	5
18	1011		α-pinene [i]	pine	1		5	
4	716		ethanethiol [i]	sulfurous, pungent			5	
13	924		thiophene [i]	sulfurous, stink, garlic			5	
24	1141	801	(*Z*)-3-hexenal [i]	grassy, leafy	25	5	1	25

21	1083	801	hexanal ^{i}	grassy, leafy	5	5	1	25
7	823	547	2-methylpropanal ^{i}	pungent	5	5	1	1
22	1090	813	1-pentanethiol ^{i}	sulfurous, pungent, baked onion		1	1	1
41	1363	991	2,4,5-trimethylthiazole ^{m}	sulfurous, vegetable		1	1	1
45	1447	908	methional ^{i}	cooked potato		1	1	1
15	971	570	2,3-butanedione ^{i}	buttery, creamy	5	5	1	
10	879		allyl mercaptan ^{i}	sulfurous, alliaceous	5		1	
49	1480	1082	diallyl disulfide ^{i}	sulfurous, alliaceous, garlic	1	1	1	
29	1183		*bis*-(1-propenyl) sulfide ^{h}	sulfurous, savory, baked onion	1		1	
40	1356		1-hexanol ^{i}	green			1	
66		1692	borneol ^{i}	woody, pine, sweet			1	
75	1854		2-vinyl-*4H*-1,3-dithiine ^{h}	raw garlic			1	
27		1002	α-terpinene ^{i}	earthy, woody		25		5
48		1120	(*Z*,*Z*)-*bis*-(1-propenyl) disulfide ^{h}	sulfurous, alliaceous, meaty		1		5
19	1075	738	dimethyl disulfide ^{i}	sulfurous, alliaceous, cabbage	1	1		1
20		895	dipropyl sulfide ^{i}	sulfurous, garlic		1		1
65		1173	2-methyl-3-(methylthio) furan ^{i}	sulfurous, vitamin B		1		1
71		1332	(*E*,*E*)-*bis*-(1-propenyl) trisulfide ^{h}	sweet, pungent		1		1
87		1283	phenylacetic acid ^{i}	floral, rose				1
12	915	633	2/3-methylbutanal ^{i}	malty, dark chocolate	25	1		
32	1241		diisopropyl disulfide ^{i}	sulfurous, meaty	5			
50	1492		(*Z*)-3-hexen-1-ol ^{i}	green, leafy	5			

30	1212	854	(*E*)-2-hexenal [i]	green, leafy	1	1
35	1299	979	1-octen-3-one [i]	mushroom	1	1
59	1577	1154	(*E*,*Z*)-2,6-nonadien-1-al [i]	sweet, cucumber	1	1
2	<500		methanethiol [f]	sulfurous, rotten	1	

[a] Numbers correspond to those in Tables 2, 3 and 4. [b] Retention indices determined by GCO on two different stationary phases (RTX-Wax and RXI-5MS). [c] Odor quality as perceived during GCO. [d] Flavor dilution (FD) factor=highest headspace volume tested (25 mL) divided by the lowest headspace volume required to detect a compound (i.e., 5, 1, 0.2, or 0.04 mL). [e] Compound was positively identified, based on retention index (RI); odor quality (O); mass spectra (MS); reference standard compound (S) and sulfur detector (SD). [f] Compound was tentatively identified by O. [g] Compound was tentatively identified by O, SD. [h] Compound was tentatively identified by RI, O. [i] Compound was tentatively identified by RI, O, S. [j] Compound was tentatively identified by RI, O, MS. [k] Compound was tentatively identified by RI, O, SD. [l] Compound was tentatively identified by RI, O, S, SD. [m] Compound was tentatively identified by RI, O, S, MS. [n] Compound was tentatively identified by RI, O, SD, MS.

Table 2. Aroma-Active Compounds in *Toona sinensis* Determined by Aroma Extract Dilution Analysis

no. [a]	*retention index* [b]		*compound*	*odor description* [c]	*FD-factor* [d]			
					raw Toona sinensis		*cooked Toona sinensis*	
	RTX-WAX	*RXI-5MS*			*RTX-WAX*	*RXI-5MS*	*RTX-WAX*	*RXI-5MS*
46	1450	1104	(*E*,*E*)-*bis*-(1-propenyl) disulfide [k]	sulfurous, cooked onion	19683	243	59049	729
47	1473	1117	(*E*,*Z*)-*bis*-(1-propenyl) disulfide [k]	sulfurous, cooked onion, roasted coffee	9	9	6561	81
61	1582	1410	*β*-caryophyllene [m]	sweet, woody	729	1	2187	81
85	2235	1411	(*Z*)-isoeugenol [i]	sweet, spicy, cloves	729	1	2187	81
87	2524	1277	phenylacetic acid [i]	floral, rose	729	9	2187	27
88	2524	1384	vanillin [i]	sweet, caramel	729	27	2187	
41	1369	989	2,4,5-trimethylthiazole [m]	sulfurous, vegetable	81	3	2187	81
28	1187		2,4-dimethylthiophene [h]	sulfurous, pungent, meaty	27		2187	

66	1688	1170	borneol [i]	woody, pine, sweet	3	27	2187	243
82	2120		cinnamyl acetate [h]	sweet, spicy	243		729	
50	1495	962	(*Z*)-3-hexen-1-ol [i]	green, leafy	27	3	729	
72	1774		unknown	sweet, woody, fruity, minty	27		729	
11	916		methyl thiirane [l]	alliaceous, pungent, garlic	1		729	
83	2149	1348	eugenol [i]	sweet, woody, cloves	81	9	243	
78	1990	1373	(*E*)-4,5-expoxy-(*E*)-2-decenal [h]	metallic, woody	27		243	3
45	1443	904	methional [l]	cooked potato	243	27	81	1
86	2331	1442	(*E*)-isoeugenol [i]	sweet, spicy, cloves	27	9	81	
44	1407		unknown	sulfurous, alliaceous, cooked	27		81	
79	2005		4-hydroxy-2,5-dimethyl-3(2*H*)-furanone [i]	pungent, sweet, caramel	27		81	
81	2066		unknown	sulfurous, garlic	9		81	
29	1211		*bis*- (1-propenyl) sulfide [h]	sulfurous			81	
69	1745		α-farnesene [j]	sulfurous, bell pepper	27		27	
35	1296	986	1-octen-3-one [i]	mushroom	3	1	27	1
18	1032	919	α-pinene [m]	pine		1	27	1
25	1150		2-methyl-2-pentenal [i]	green, juicy	81		9	
53	1521	1191	2-isobutyl-3-methoxypyrazine [h]	sulfurous, bell pepper	27	9	9	3
33	1278	1081	dibutyl sulfide [i]	sulfurous, green	1	9	9	
58	1558		unknown	woody, pine	729		3	
55	1543	1096	linalool [i]	floral, sweet, lemon	243	9	3	9
80	2024		unknown	pungent, sweaty	243		3	
24	1150	801	(*Z*)-3-hexenal [m]	grassy, leafy	81	243	3	3

64	1660	868	3-methylbutanoic acid ^{i}	cheesy, sweaty	81	9	3	
15	986	575	2,3-butanedione ^{h}	buttery, creamy	9	27	3	
12	933	646	2/3-methylbutanal ^{i}	malty, dark chocolate	9	9	3	
36	1324	930	2-acetyl-1-pyrroline ^{i}	rice, roasty	9	1	3	
37	1353		2-isopropyl-4-methylthiazole ^{h}	sulfurous, stink	1		3	
84	2193	1318	*p*-vinylguaiacol ^{j}	sweet, woody, cloves	27	27	1	729
77	1939	1537	cubebol ^{i}	spicy, minty	27	27	1	81
43	1389		(*E*,*E*)-2,4-hexadienal ^{i}	sweet, cucumber	3		1	
4	724		ethanethiol ^{i}	sulfurous, pungent	1		1	
22	1093	829	1-pentanethiol ^{i}	sulfurous, pungent, baked onion			1	1
34	1286		α-terpinolene ^{h}	woody, terpene			1	
21	1086	801	hexanal ^{l}	grassy, leafy	243	243		
74	1841	1257	geraniol ^{m}	floral, lemon	81	1		
42	1379		dimethyl trisulfide ^{j}	sulfurous, cooked cabbage	27			
76	1896		phenethyl alcohol ^{i}	sweet, rose	27			
62	1611		butanoic acid ^{j}	cheese, sweaty	9			
32	1257	1015	diisopropyl disulfide ^{h}	sulfurous, meaty	3			27
27	1168	1001	α-terpinene ^{i}	earthy, woody	1	1		
30	1194	856	(*E*)-2-hexenal ^{i}	green, leafy	1	1		
19		743	dimethyl disulfide ^{m}	sulfurous, alliaceous, cabbage		1		243
70		1310	diallyl trisulfide ^{l}	sulfurous, alliaceous		3		27
8		579	diethyl sulfide ^{i}	garlic				3
20		899	dipropyl sulfide ^{i}	sulfurous, garlic		9		1
65		1159	2-methyl-3-(methylthio) furan ^{i}	sulfurous, vitamin B		1		1

40	874	1-hexanol [m]	green	9
54	1092	(*Z*)-6-nonenal [i]	sweet, green, cucumber	9
16	693	methyl allyl sulfide [i]	garlic	1
59	1152	(*E*,*Z*)-2,6-nonadien-1-al [i]	sweet, cucumber	1

[a] Numbers correspond to those in records in Tables 1, 3 and 4. [b] Retention indices determined by GCO on two different stationary phases (RTX-Wax and RXI-5MS). [c] Odor quality as perceived during GCO. [d] Flavor dilution (FD) factor, determined on both RTX-Wax and RXI-5MS columns. [e-n] See Table 1.

Table 3. Aroma-Active Compounds in *Toona sinensis* Determined by Headspace Solid-Phase Microextraction

no.[a]	*retention index* [b]		*compound*	*odor description* [c]	*raw Toona sinensis* [d]		*cooked Toona sinensis*	
	RTX-WAX	*RXI-5MS*			*DB-WAX*	*HP-5MS*	*DB-WAX*	*HP-5MS*
1	545	<500	hydrogen sulfide [g]	rotten egg	+ [o]	+	+	+
3	703		acetaldehyde [m]	pungent, yogurt	+	-	-	-
6	787		propanal [j]	pungent, sweet	-	-	+	-
7	822	536	2-methylpropanal [i]	pungent	+	+	+	+
10		556	allyl mercaptan [i]	sulfurous, alliaceous	-	+	-	+
11	921	612	methyl thiirane [e]	alliaceous, pungent	+	+	+	+
14		789	isopropyl sulfide [i]	sulfurous, rubbery	-	-	-	+
17	1008	725	methyl 1-propenyl sulfide [j]	pungent, meaty	+	+	+	- [p]
18	1016	917	α-pinene [m]	pine	+	+	+	+
21	1073	797	hexanal [m]	grassy, leafy	+	+	-	-
22	1093		1-pentanethiol [i]	sulfurous, pungent, baked onion	-	-	+	-
23	1106	974	β-pinene [m]	pine	-	+	+	+

24	1134	797	(*Z*)-3-hexenal [m]	grassy, leafy	+	+	-	-
26	1159		2,5-dimethyl thiophene [i]	sulfurous, garlic	-	-	+	-
28	1186	869	2,4-dimethyl thiophene [j]	sulfurous, pungent, meaty	+	+	-	+
29	1206	909	*bis*-(1-propenyl) sulfide [n]	sulfurous, baked onion, savory	+	+	+	+
30	1206	854	(*E*)-2-hexenal [m]	green, leafy	+	+	-	-
31	1250	901	3,4-dimethyl thiophene [n]	sulfurous, savory, roasted onion	+	+	+	+
32		1020	diisopropyl disulfide [i]	alliaceous	-	+	-	+
33	1267		dibutyl sulfide [i]	sulfurous, green	+	-	-	-
35		980	1-octen-3-one [i]	mushroom	-	-	-	+
37		1028	2-isopropyl-4-methyl thiazole [i]	sulfurous, stink	-	+	-	+
38	1350		mercaptoacetone [j]	alliaceous, garlic	+	-	-	-
39	1364	842	4,5-dimethyl thiazole [i]	alliaceous, stink	+	+	+	+
40		862	1-hexanol [i]	green	-	+	-	+
41	1375		2,4,5-trimethyl thiazole [m]	sulfurous, vegetable	±	-	-	-
45	1440	909	methional [l]	cooked potato	+	+	+	+
46	1448	1094	(*E*,*E*)-*bis*-(1-propenyl) disulfide [n]	sulfurous, cooked onion	+	+	+	+
47	1470	1104	(*E*,*Z*)-*bis*-(1-propenyl) disulfide [n]	sulfurous, cooked onion, roasted coffee	+	+	+	+
48	1473	1128	(*Z*,*Z*)-*bis*-(1-propenyl) disulfide [n]	sulfurous, alliaceous, meaty	+	+	-	-
50	1497	964	(*Z*)-3-hexen-1-ol [i]	green, leafy	+	+	+	+
51	1492		unknown	sulfurous, alliaceous	+	-	+	-
52	1498	1376	α-copaene [j]	woody, floral	+	-	+	+
53	1525		2-isobutyl-3-methoxypyrazine [h]	sulfurous, bell pepper	+	-	+	-

55	1539	1100	linalool [i]	floral, sweet, lemon	+	-	-	+
56	1543		(*Z*)-(1-propenyl) propanedithioate [j]	sulfurous, green	+	-	-	-
57	1554	1167	(*E*)-(1-propenyl) propanedithioate [j]	sulfurous, stink, alliaceous	+	+	+	+
59	1576		(*E*,*Z*)-2,6-nonadien-1-al [i]	sweet, cucumber	+	-	+	-
60	1592	1387	*β*-elemene [j]	earthy, sweet	+	+	+	-
61	1603		*β*-caryophyllene [m]	sweet, woody	+	-	+	-
63	1634	1135	(*Z*)-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene [n]	sulfurous, alliaceous, stink	+	+	+	+
66		1149	borneol [i]	woody, pine, sweet	-	+	-	+
67	1683	1182	(*E*)-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene [n]	sulfurous, alliaceous, bell pepper	+	+	+	+
68		1189	*α*-terpinenol [h]	woody, sweet	-	+	-	+
69	1743		*α*-farnesene [j]	sulfurous, bell pepper	+	-	+	-
71		1338	(*E*,*E*)-*bis*-(1-propenyl) trisulfide [n]	sweet, pungent	-	+	-	+
73	1820		anethole [j]	sweet, caramel, wood	-	-	+	-
83		1347	eugenol [i]	sweet, woody	-	+	-	+
85	2221		(*Z*)-isoeugenol [i]	sweet, wool	+	-	+	-
86	2356	1458	(*E*)-isoeugenol [i]	wood, medicine	+	+	+	-
87		1285	phenylacetic acid [i]	floral, rose	-	-	-	+

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[a] Numbers correspond to those in records in Tables 1, 2 and 4. [b] Retention indices determined by GCO on two different stationary phases (DB-Wax and HP-5MS). [c] Odor quality as perceived during GCO. [d] The existence of compounds in TS. [e-n] See Table 1. [o] + = Compound was detected. [p] - = Compound was not detected.

Table 4.
Effect of GC injection temperature on formation/loss of selected potent sulfur compounds found in raw *Toona sinensis*

no.[a]	*Compound*	*Abundance* [b]			
		Inlet temperature			
		175℃	*200℃*	*225℃*	*250℃*
46	(*E*,*E*-*bis*-(1-propenyl) disulfide	86087896	68518024	48465304	24841002
47	(*E*,*Z*)-*bis*-(1-propenyl) disulfide	81637352	64375732	41366300	14978116
48	(*Z*,*Z*)-*bis*-(1-propenyl) disulfide	24428810	14513904	n.d. [c]	n.d.
63	(*Z*)-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene	82596992	83482848	84969720	88506728
67	(*E*)-2-mercapto-3,4-dimethyl-2,3-dihydrothiophene	61152128	72100624	78918704	83417160
31	3,4-dimethylthiophene	5092681	11609610	29164902	48546516

[a] Numbers correspond to those in Tables 1, 2 and 3. [b] Total ion (peak) abundance for compound isolated from *Toona sinensis* by SPME as a function of increasing inlet temperature; [c] No peak was detected.

HIGHLIGHTS

- Aroma components of raw and cooked *Toona sinensis* (A. Juss.) M. Roem. were identified
- Highly volatile aroma compounds were determined by static headspace dilution analysis
- Odorants of intermediate and semi-volatilies were analyzed by aroma extract dilution analysis
- Potent and characteristic sulfur compounds in *Toona sinensis* were positively identified