



## Short Communication

## Pungent and volatile constituents of dried Australian ginger

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## ABSTRACT

Ginger is well known for its pungent flavour and health-benefitting properties, both of which are imparted by various gingerol derivatives and other volatile constituents. Although there has been a considerable amount of research into the chemical constituents found in fresh ginger, there is little information available on the quality of Australian-grown dried ginger, particularly that intended for processing purposes. Here, we investigate differences in the chemical composition of three samples of processing-grade ginger, ranging from very poor to good quality. Gingerols and 6-shogaol were quantified using high performance liquid chromatograph (HPLC), while gas chromatography coupled with mass spectrometry (GC-MS) was used to identify and semi-quantify the volatile constituents and other gingerol derivatives. Significant differences were found between the samples in their content of gingerols and [6]-shogaol, as well as in their total phenolic content and antioxidant capacity. A total of 100 volatile compounds were identified in the dried ginger samples, including 54 terpenoid derivatives and 35 gingerol derivatives. Several compounds are reported from ginger for the first time, including limonene glycol and neryl laurate. In addition, we provide the second report of the presence of shyobunol, geranyl-p-cymene and geranyl- $\alpha$ -terpinene in ginger.

## 1. Introduction

The rhizomes of ginger (*Zingiber officinale* Roscoe) are characterised by a pungent flavour, resulting from the presence of gingerol compounds (Kumara et al., 2017), the most abundant of which are [6]-gingerol, [8]-gingerol and [10]-gingerol (Yudthavorasit et al., 2014). Furthermore, numerous derivatives of gingerols are also present in fresh and dried ginger, including shogaols and paradols (Jolad et al., 2004, 2005; Yudthavorasit et al., 2014). In combination with some of these derivatives, gingerols are reported to provide most of the documented medicinal properties of ginger (Govindarajan and Connell, 1983; Grzanna et al., 2005; Kubra and Rao, 2012), as well as its characteristic pungent taste and odour (Fisher and Scott, 2007).

When fresh ginger is dried, gingerols are converted to their respective shogaols (alkene side chain derivatives) through an elimination dehydration reaction (Ghasemzadeh et al., 2018; Huang et al., 2011; Wohlmuth et al., 2005). The proportion of gingerols converted to shogaols depends on the drying temperature, but can approach ~50% conversion under very high drying temperatures (180 °C) (Ghasemzadeh et al., 2018). As shogaols are twice as pungent as gingerols (Narasimhan & Govindarajan, 1978), this increases the pungency of dried

ginger proportionally. Furthermore, shogaols also show higher bioactive and medicinal properties (Ghasemzadeh et al., 2018) compared to their respective gingerols (Wei et al., 2005).

[6]-paradol, the alkane derivative of [6]-shogaol, can be formed from [6]-shogaol through enzymatic reduction of the alkene bond (Jo et al., 2016), although little has been published on the purported synthesis pathway in ginger. [6]-paradol is present in fresh and dried ginger (Jolad et al., 2005; Nagendra chari et al., 2013), albeit at much lower concentrations compared to the gingerols and shogaols. However, it possesses greater bioavailability and neuroprotective effects compared to 6-shogaol (Choi et al., 2017; Park et al., 2016; Sapkota et al., 2019). Other reported health benefits of [6]-paradol include anti-tumour activity (Chung et al., 2001; Lee and Surh, 1998; Surh et al., 1999), anti-inflammatory activity (Ilic et al., 2014; Saptarini, 2013) and upregulation of metabolic activity and glucose usage providing anti-hyperglycaemic activity (Iwami et al., 2011; Wei et al., 2017). Whilst many of these bioactive properties can also be imparted by gingerols and shogaols, they are slightly less potent compared to the corresponding paradols. Notably, Chen et al. (2012) demonstrated that shogaols are metabolised to paradols in rats, suggesting that consumption of shogaols may have more beneficial health effects than that

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anticipated from *in vitro* studies on the bioactivity of shogaols.

Previous studies have investigated the volatile constituents of fresh and dried ginger (Jolad et al., 2004, 2005), profiled the variation between different varieties and growing locations (Bailey-Shaw et al., 2008; Wohlmuth et al., 2005), and determined the effects of processing methods such as drying on these constituents (Bartley and Jacobs, 2000). However, there is limited information available on the chemical composition of dried processing-grade ginger, and even fewer studies correlating variations in the chemical constituents with the perceived quality of the ginger. To this end, we characterise the major pungent and volatile constituents of three samples of dried Australian processing-grade ginger.

## 2. Material and methods

### 2.1. Sample processing

Three samples of Queensland-grown processing-grade fresh ginger from three different growing years (2017, 2018 and 2019) were dried and powdered. Based on anecdotal information and organoleptic testing, these samples were identified as being low quality (2017 sample), average quality (2018) and high quality (2019).

### 2.2. Extraction protocols

Polar compounds, such as gingerols and their derivatives, were extracted from the dried ginger samples using the extraction protocol previously reported by our laboratory for the extraction of phenolics (Johnson et al., 2019, 2020a, 2020b). Briefly approximately 0.5 g of dried ginger was combined with 7 mL of 90% aqueous methanol and shaken end-over-end for 60 min. After centrifuging (1000 g; 10 min) and collecting the supernatant, this was repeated with another 7 mL of fresh 90% methanol. The two supernatants were combined and volumetrically made up to 15 mL. Extracts were prepared in triplicate, with results expressed in mg kg<sup>-1</sup> (as-is basis). These extracts were used for HPLC profiling of gingerol and its derivatives as well as measuring the total antioxidant and phenolic contents.

To extract the volatile compounds for GC-MS analysis, most of which are relatively non-polar in nature, a separate extract was prepared. A portion of ginger powder (0.3000 ± 0.0001 g) was weighed into a glass vial, to which 5 mL of dichloromethane (DCM) was added. The vials were sonicated for 30 min (Soniclean 160TD ultrasonic cleaner; Dudley Park, South Australia) before the supernatant was syringe filtered (0.45 µm PTFE; Livingstone) into mass spectrometry-grade GC-MS vials (Shimadzu).

### 2.3. Measurement of total phenolics and total antioxidant content

Total phenolics (TP) were measured in the polar methanolic extracts using the Folin-Ciocalteu method of Singleton and Rossi (1965). The total antioxidant content was estimated using the CUPRAC (cupric reducing antioxidant capacity) assay of Apak et al. (2013). The results were quantified as equivalents of gallic acid (GA) and Trolox equivalents (TE), respectively. Both methods have been previously described by our laboratory (Johnson et al., 2020a, 2020b, 2020c).

### 2.4. Gingerol profiling by HPLC

Gingerol profiling was performed on the polar extracts using high-performance liquid chromatography (HPLC), following an in-house method previously developed by our laboratory for the analysis of these constituents in dried ginger samples (unpublished data). The 90% methanol extracts were syringe filtered (0.45 µm PTFE; Livingstone) before being directly injected without any further preparation. The separation and quantification of gingerols and 6-shogaol was achieved on an Agilent 1100 HPLC system, comprising a G1313A autosampler,

G1322A vacuum degasser, G1311A quaternary pump, G1316A thermostatted column compartment and G1365B multi-wavelength detector module. A reversed phase C<sub>18</sub> column was used (Agilent Eclipse XDB-C18; 150 × 4.6 mm; 5 µm pore size) with the column temperature controlled at 27 ± 0.8 °C. An injection volume of 5 µL was used, while a wavelength of 230 nm was used for the quantification of gingerols and 6-shogaol.

A gradient mobile phase of water (A) and methanol (B) was used, beginning at 30% B (0 min), ramping to reach 60% B by 2 min, 63% by 10 min, 65% by 16 min and 100% at 28 min, before holding for a further 5 min. The sample run time was 33 min, followed by a flushing period of 5 min, making an overall run time of 38 min per sample. A flow rate of 1 mL/min was used throughout.

The peaks of interest were identified using authentic standards of [6]-gingerol (Toronto Research Chemicals; Toronto, Canada), [8]-gingerol (Glentham Life Sciences; Corsham, United Kingdom), [10]-gingerol (Glentham Life Sciences) and [6]-shogaol (Toronto Research Chemicals), as well as through their UV spectral characteristics. Standard curves of these four compounds were prepared in methanol (10–100 mg L<sup>-1</sup>) for quantification purposes. All standard curves showed high linearity (R<sup>2</sup> = 0.9991–0.9998), with the detector response factors ranging between 4.29 (for [10]-gingerol) to 27.32 (for [6]-shogaol). The typical repeatability of the analysis (for [6]-gingerol) from consecutive injections was 0.10% relative standard deviation (RSD) in the peak area, while the inter-day precision was 0.31% for retention time and 2.02% for peak area (from four injections over the course of a week). Triplicate injections of the sample ginger extract also showed high repeatability (RSD of 0.24% for [6]-gingerol, 0.32% for [8]-gingerol, 0.63% for [10]-gingerol and 0.24% for [6]-shogaol).

### 2.5. GC-MS analysis

In addition to the pungent gingerols and their derivatives, volatile compounds also play a large role in determining the organoleptic properties and hence the perceived flavour of ginger. Gas chromatography coupled with mass spectrometry (GC-MS) was used to profile the volatile compounds present in the previously described DCM extracts. Although no internal standard was used, care was taken to ensure that the same mass of powdered ginger sample was used in each extraction (±0.0001 g), allowing for semi-quantification of each constituent by its peak area on the total ion chromatogram (TIC).

GC-MS analysis was performed on a Shimadzu QP2010 Plus system fitted with an autoinjector/autosampler (AOC-20i/s) and a Shimadzu SH-Rxi-5Sil MS column (29 m × 0.25 mm i.d. × 0.25 µm thickness). Three solvent rinses (in DCM) were performed pre- and post-injection, with two rinses of the needle with the extract prior to injection. The injection volume was 0.5 µL using split mode (split ratio = 15) and an injection temperature of 250 °C. Helium was used as a carrier gas, at a column flow rate of 1.31 mL/min and pressure of 73.2 kPa. The oven temperature began at 50 °C, ramped at 10 °C/min until 130 °C, slowed to 5 °C/min until 200 °C, then returned to a ramp of 10 °C/min until 340 °C, where it held for 3 min to remove any residue from the column. The total run time was 39 min. The ion source and mass spectrometer interface temperatures were both set at 200 °C. The mass spectrometer was set to scanning mode, with acquisition (35–500 m/z) between 2.5 and 37 min. For quantitative purposes, peaks on the total ion chromatogram (TIC) were integrated if their slope was >1000 counts/min and their peak height was >100,000 counts. Compounds were identified from comparison of their mass spectra to the NIST library (<https://chemdata.nist.gov/>) and from their linear retention indices (LRIs), calculated from their retention times compared against a set of C<sub>8</sub>–C<sub>30</sub> alkane standards, following the method of van Den Dool and Kratz (1963).

### 2.6. Data analysis

Statistical testing was performed in IBM SPSS v. 26 (New York, USA).

As all data was approximately normally distributed, one-way ANOVAs were used to compare data between different samples, followed up by post-hoc Tukey testing (at  $\alpha = 0.05$ ) if a significant result was returned. Plots were created in Microsoft Excel. Where applicable, results are presented as mean  $\pm$  1 standard deviation.

### 3. Results and discussion

#### 3.1. Antioxidant properties and pungent constituents

The total phenolic content and total antioxidant capacity of the dried ginger samples showed a consistent trend, from lowest in the oldest ginger sample (2017) to highest in the 2019 sample (Table 1). However, the difference between the 2018 and 2019 samples was not significantly different. The [6]-gingerol content was significantly different between samples, with the lowest levels in the 2017 ginger and highest in the 2019 ginger (see Fig. 1). For both [8]-gingerol and [10]-gingerol, no significant differences in concentration were found between the 2017 and 2018 samples, while the 2019 sample had significantly higher levels of both compounds. The [6]-shogaol content did not appear to show any clear changes with age, being lowest in the 2019 ginger and highest in the 2018 ginger, but remaining relatively low in the 2017 ginger. However, the ratio of [6]-gingerol to [6]-shogaol did decrease significantly with the sample age, indicating that the youngest (2019) sample contained significantly higher levels of [6]-gingerol compared to its [6]-shogaol content.

The lack of a clear trend in [6]-shogaol content with increasing age of the sample was consistent with previous research by our laboratory (Johnson et al., 2020d), which found no significant increase in [6]-shogaol with aging, but rather suggested that the equilibrium point for the dehydration of [6]-gingerol into [6]-shogaol may be dependent upon the drying conditions, rather than on the [6]-gingerol concentration. In other words, younger dried ginger samples contained approximately the same amount of [6]-shogaol as the older samples, irrespective of their higher [6]-gingerol levels.

#### 3.2. GC-MS: volatile constituents

The GC-MS profiling of the ginger samples revealed the presence of 100 volatile compounds which were identified from their mass spectral data and linear retention indices (see Supplementary Materials; Table SM1). A total of 54 terpenoid-related compounds were identified, comprising 20 monoterpenes, 27 sesquiterpenes, and 7 diterpenes (Table SM1; Fig. 2).

The majority of volatile constituents presented in this work had been reported by previous authors (e.g. Chen and Ho, 1988; Cornell and Jordan, 1971; Dhanik et al., 2017; Jiang et al., 2006; Nishidono et al., 2020; Wohlmuth et al., 2006). However, the sesquiterpene shyobunol has only been reported in ginger from Iraq by Shareef et al. (2016).

Although both *p*-cymene (Nigam et al., 1964; Smith and Robinson, 1981; Wohlmuth et al., 2006) and geraniol (Baldin et al., 2019;

Jayashree et al., 2014) have been reported in ginger by numerous researchers, geranyl-*p*-cymene has only recently been reported by Hazim et al. (2020) from fresh ginger. Similarly, geranyl- $\alpha$ -terpinene was only identified from ginger oil by Ismaeel and Usman (2021). In this work, we also tentatively identified the presence of isomers of shyobunol and geranyl- $\alpha$ -terpinene in the ginger samples.

Other compounds that have been identified in this work, which do not appear to have been previously reported in ginger, included limonene glycol and neryl laurate (Table SM1). Limonene glycol has been found in a variety of plants, including oil from the conifer *Torreya grandis* (Niu et al., 2010) and cardamom oil (Núñez-Carmona et al., 2018). This compound can be produced from the hydrolysis of limonene oxide, which in turn is produced by the oxidation of limonene. D-limonene was detected in the ginger samples (Table SM1), indicating the potential origin of limonene glycol in this matrix. In contrast, neryl laurate has only been reported from a few species, including *Rosa damascena* (Ansari et al., 2017) and possibly from *Cedrus atlantic* (Ainane et al., 2019). However, the related ester neryl butyrate is a common constituent from volatile oils derived from aromatic plants (de Carvalho et al., 2020).

In addition, several compounds were tentatively identified from ginger for the first time, including hydroxycitronellol – previously found in the herb *Pelargonium crispum* (Sadgrove, 2018) and *Citrus junos* (Park et al., 2004), dihydrofarnesol – previously reported from fragrant orchids (Julsrigual et al., 2013) and *Cyclamen* spp. (Shibusawa et al., 2018), and 4,6-bis(4-methylpent-3-en-1-yl)-6-methylcyclohexa-1,3-diene-carbaldehyde – previously known from the marine bryozoan *Flustra foliacea* (Peters et al., 2002). However, as suggested by Holst et al. (1994), this latter compound may potentially be produced from the condensation of citral during the extraction or analysis process, rather than being naturally found in the original sample matrix.

Forty-two of the major peaks were selected for quantification and comparison purposes between the three ginger samples, comprising 5 monoterpenes, 14 sesquiterpenes, 3 diterpenes and 20 gingerol-related compounds (termed ‘gingerol derivatives’) (Table 2). Relatively, the 2018 ginger sample had the highest levels of volatiles extracted (summed peak area of 14.9 million arbitrary units), followed by the 2017 sample (9.6 million arbitrary units). The 2019 ginger sample containing the least volatiles (summed peak area of 8.6 million arbitrary units).

For the monoterpenes, the 2018 ginger had the highest levels of  $\beta$ -citronellol, geraniol, geranyl acetate and corymbolone. The 2017 sample also had a relatively high content of corymbolone, but low levels of  $\beta$ -citronellol. Within the sesquiterpenes, notable differences between the three samples were observed for  $\alpha$ -curcumene, trans-sesquisabinene hydrate and  $\beta$ -sesquiphellandrene. For most of the remaining volatiles, the proportion of each compound was comparable to that found in the other samples.

#### 3.3. GC-MS: pungent compounds

In terms of the gingerol-related (pungent) compounds, a total of 35 gingerols and gingerol derivatives were identified, as well as 5 methoxyphenols with a related structure to gingerol. All of the gingerol derivatives were previously identified by Jolad et al. (2005) in dried ginger or by Nishidono et al. (2020) in fresh ginger. The presence of [10]-isoshogaol was notable, as this compound has only been previously reported from ginger by a limited number of authors (Nishidono et al., 2020; Zhan et al., 2008), likely due to its very low concentrations. For example, the average concentration of [6]-shogaol across the samples was found to be  $48.8 \pm 5.4$  (n = 3) times higher than its isomeric form, [6]-isoshogaol, indicating high favourability toward the more conjugated and more stable isomer of [6]-shogaol. This trend would likely hold true for other isoshogaols, such as [10]-isoshogaol. Similarly, [6]-gingerdiol-(2E)-geranial acetal appears to have only been previously identified by a few authors (Jolad et al., 2005; Nishidono et al., 2020).

The proportions of most of the pungent constituents were similar between the three samples. The largest differences in the relative

**Table 1**

Physical and chemical characteristics of the three powdered ginger samples.

| Parameter                                         | 2017 ginger                  | 2018 ginger                  | 2019 ginger                  |
|---------------------------------------------------|------------------------------|------------------------------|------------------------------|
| Total phenolics/mg GAE 100g <sup>-1</sup> (n = 3) | 1834 $\pm$ 106 <sup>a</sup>  | 2654 $\pm$ 434 <sup>b</sup>  | 3193 $\pm$ 297 <sup>b</sup>  |
| CUPRAC/mg TE 100g <sup>-1</sup> (n = 3)           | 3106 $\pm$ 287 <sup>a</sup>  | 4932 $\pm$ 244 <sup>b</sup>  | 5440 $\pm$ 20 <sup>b</sup>   |
| [6]-gingerol/mg kg <sup>-1</sup> (n = 3)          | 2215 $\pm$ 101 <sup>a</sup>  | 3491 $\pm$ 26 <sup>b</sup>   | 5383 $\pm$ 270 <sup>c</sup>  |
| [8]-gingerol/mg kg <sup>-1</sup> (n = 3)          | 674 $\pm$ 46 <sup>a</sup>    | 764 $\pm$ 17 <sup>a</sup>    | 1167 $\pm$ 59 <sup>b</sup>   |
| [10]-gingerol/mg kg <sup>-1</sup> (n = 3)         | 1475 $\pm$ 127 <sup>a</sup>  | 1524 $\pm$ 42 <sup>a</sup>   | 2065 $\pm$ 58 <sup>c</sup>   |
| [6]-shogaol/mg kg <sup>-1</sup> (n = 3)           | 836 $\pm$ 50 <sup>b</sup>    | 1063 $\pm$ 19 <sup>c</sup>   | 709 $\pm$ 15 <sup>a</sup>    |
| Ratio of [6]-gingerol:[6]-shogaol                 | 2.65 $\pm$ 0.08 <sup>a</sup> | 3.28 $\pm$ 0.04 <sup>b</sup> | 7.59 $\pm$ 0.36 <sup>c</sup> |

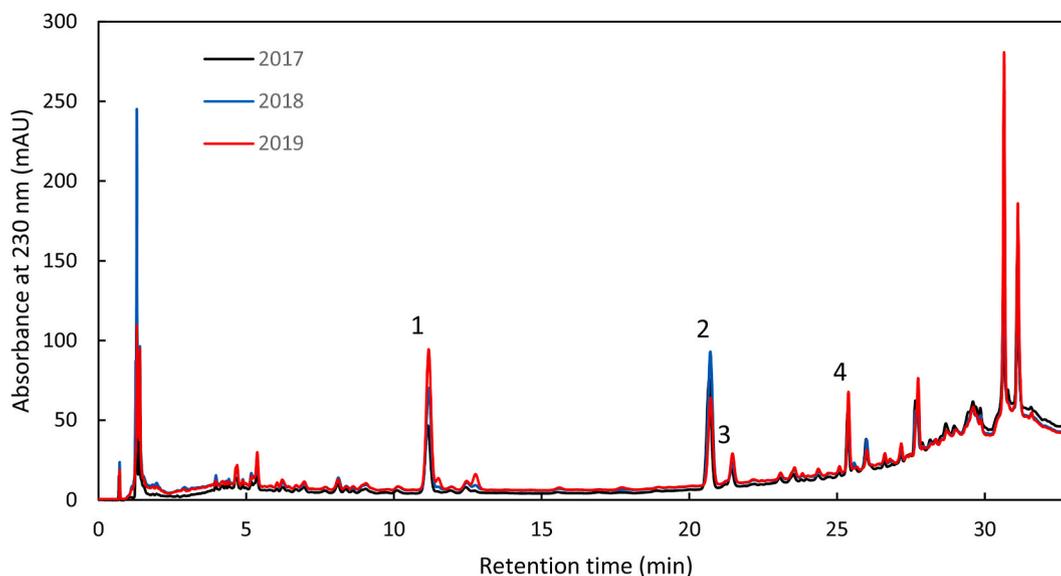


Fig. 1. HPLC chromatograms of the three powdered ginger samples. The labelled peaks are (1) [6]-gingerol, (2) [6]-shogaol, (3) [8]-gingerol and (4) [10]-gingerol.

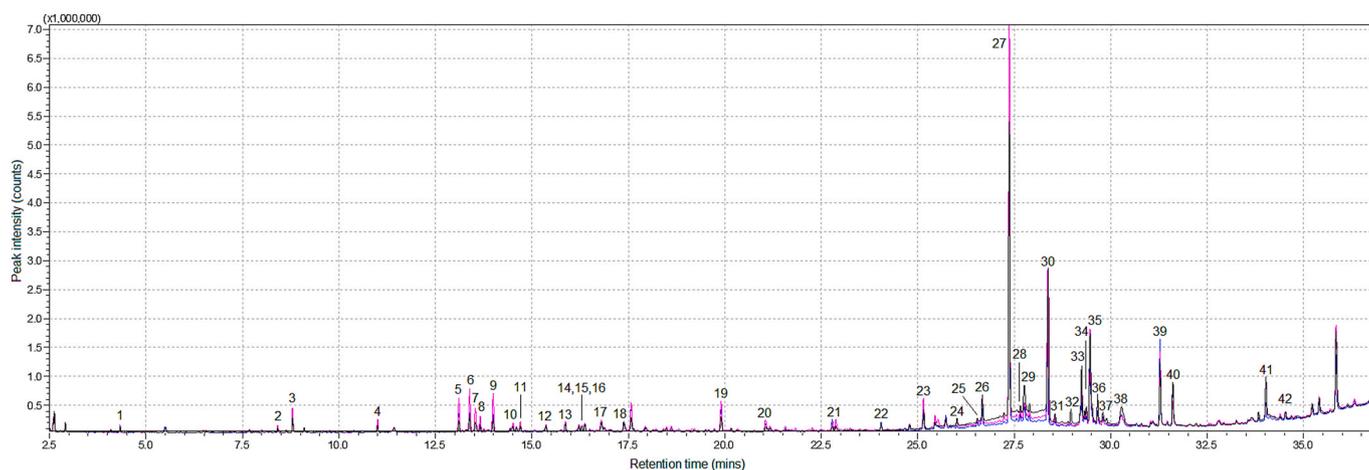


Fig. 2. The total ion chromatogram of the three ginger samples. Black = 2019, pink = 2018, blue = 2017. Compound numbers correspond to those provided in Table 2. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

proportions of the pungent constituents was found for acetoxy-[6]-gingerol, followed by [4]-gingerol, [10]-gingerdione and methyl-[6]-shogaol. In contrast, the proportions of diacetoxy-[6]-gingerdiol and the 5-acetoxy-[6]-gingerdiol isomer were quite consistent between samples.

The 2019 ginger had the highest proportion of [6]-gingerol (12.5% of the total peak area) and the lowest proportion of [6]-shogaol (18.5%). After [6]-shogaol and [6]-gingerol, the next greatest constituent was diacetoxy-[6]-gingerdiol, which comprised between 7.4 and 8.7% of the total peak area. [10]-shogaol was also present in relatively high concentrations (4.2–7.0% of the total peak area).

#### 4. Conclusion

Significant differences were found between the three ginger samples in their pungent components, as well as in the volatile terpenes present. The 2019 sample contained much higher levels of 6-gingerol and possessed a higher 6-gingerol:6-shogaol ratio. A total of 54 terpenoid derivatives were identified in the dried ginger samples, alongside 35 gingerol derivatives. Several compounds are reported from ginger for the first time. Further research is recommended to allow the correlation

of specific compounds with specific aspects of ginger flavour and quality.

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#### CRediT authorship contribution statement

**Joel B. Johnson:** Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing – original draft, Writing – review & editing. **Janice S. Mani:** Investigation, Writing – review & editing. **Simon White:** Resources, Writing – review & editing. **Philip Brown:** Resources, Writing – review & editing. **Mani Naiker:** Conceptualization, Funding acquisition, Project administration, Resources, Supervision, Writing – review & editing.

**Table 2**

GC-MS profiles of the major volatile and pungent constituents of the three dried ginger samples. Data are given as percent of total peak area in each chromatogram. Compound numbers correspond to the chromatogram in Fig. 2.

| #                                  | R <sub>t</sub><br>(min) | LRI  | Lit<br>LRI* | M <sup>+</sup><br>(m/z) | Base peak<br>(m/z) | Compound                                                                            | Class               | 2017<br>ginger (%) | 2018<br>ginger (%) | 2019<br>ginger (%) |
|------------------------------------|-------------------------|------|-------------|-------------------------|--------------------|-------------------------------------------------------------------------------------|---------------------|--------------------|--------------------|--------------------|
| 1                                  | 4.33                    | 953  | 953         | 136                     | 93                 | Camphene                                                                            | Monoterpene         | 0.38               | 0.27               | 0.24               |
| 2                                  | 8.41                    | 1223 | 1228        | 156                     | 69                 | β-citronellol                                                                       | Monoterpene         | 0.18               | 0.30               | 0.21               |
| 3                                  | 8.80                    | 1247 | 1245        | 154                     | 69                 | Geraniol                                                                            | Monoterpene         | 0.95               | 1.03               | 0.73               |
| 4                                  | 11.00                   | 1374 | 1376        | 196                     | 69                 | Geranyl acetate                                                                     | Monoterpene         | 0.64               | 0.64               | 0.35               |
| 5                                  | 13.11                   | 1482 | 1483        | 202                     | 132                | α-curcumene                                                                         | Sesquiterpene       | 1.40               | 1.89               | 0.69               |
| 6                                  | 13.39                   | 1496 | 1495        | 204                     | 119                | Zingiberene                                                                         | Sesquiterpene       | 1.42               | 2.49               | 1.19               |
| 7                                  | 13.53                   | 1503 | 1504        | 204                     | 93                 | α-farnesene                                                                         | Sesquiterpene       | 0.67               | 1.44               | 0.82               |
| 8                                  | 13.66                   | 1509 | 1509        | 204                     | 69                 | β-bisabolene                                                                        | Sesquiterpene       | 0.56               | 0.93               | 0.34               |
| 9                                  | 13.99                   | 1525 | 1518        | 204                     | 69                 | β-sesquiphellandrene                                                                | Sesquiterpene       | 1.41               | 2.31               | 0.83               |
| 10                                 | 14.51                   | 1550 | 1547        | 222                     | 59                 | Elemol                                                                              | Sesquiterpene       | 0.54               | 0.55               | 0.41               |
| 11                                 | 14.70                   | 1559 | 1556        | 222                     | 69                 | trans-nerolidol                                                                     | Sesquiterpene       | 0.51               | 0.58               | 0.37               |
| 12                                 | 15.36                   | 1591 | 1588        | 222                     | 69                 | cis-sesquisabinene hydrate                                                          | Sesquiterpene       | 0.43               | 0.42               | 0.41               |
| 13                                 | 15.87                   | 1614 | 1620        | 222                     | 69                 | Zingiberenol                                                                        | Sesquiterpene       | 0.67               | 0.63               | 0.62               |
| 14                                 | 16.22                   | 1631 | 1638        | 222                     | 69                 | trans-sesquisabinene hydrate                                                        | Sesquiterpene       | 0.39               | 0.48               | 0.60               |
| 15                                 | 16.29                   | 1635 | 1622        | 222                     | 121                | Epiglobulol                                                                         | Sesquiterpene       | 0.30               | 0.42               | 0.27               |
| 16                                 | 16.37                   | 1638 | 1638        | 194                     | 137                | Zingerone                                                                           | Gingerol            | 0.50               | 0.55               | 0.60               |
| 17                                 | 16.80                   | 1658 | 1654        | 222                     | 59                 | β-eudesmol                                                                          | Sesquiterpene       | 0.92               | 0.97               | 0.80               |
| 18                                 | 17.38                   | 1686 | 1687        | 222                     | 137                | Shyobunol                                                                           | Sesquiterpene       | 1.01               | 0.99               | 0.93               |
| 19                                 | 19.90                   | 1805 | 1781        | 272                     | 69                 | α-springene                                                                         | Diterpene           | 2.09               | 2.08               | 1.29               |
| 20                                 | 21.06                   | 1862 | 1853        | 236                     | 109                | Corymbolone                                                                         | Monoterpene         | 0.87               | 1.01               | 0.54               |
| 21                                 | 22.78                   | 1952 | 1980        | 270                     | 119                | Geranyl-p-cymene                                                                    | Diterpene           | 1.05               | 0.54               | 0.46               |
| 22                                 | 24.05                   | 2029 | 2033        | 290                     | 69                 | Geranyl linalool                                                                    | Diterpene           | 0.66               | 0.35               | 0.45               |
| 23                                 | 25.15                   | 2109 | 2113        | 286                     | 137                | Tentative: 4,6-bis(4-methylpent-3-en-1-yl)-6-methylcyclohexa-1,3-diene-carbaldehyde | Sesquiterpene       | 1.69               | 1.81               | 1.29               |
| 24                                 | 26.02                   | 2172 | 2183        | 266                     | 137                | [4]-gingerol                                                                        | Gingerol derivative | 0.14               | 0.31               | 0.49               |
| 25                                 | 26.54                   | 2214 | 2224        | 276                     | 137                | [6]-isoshogaol                                                                      | Gingerol derivative | 0.51               | 0.40               | 0.41               |
| 26                                 | 26.67                   | 2226 | 2235        | 278                     | 137                | [6]-paradol                                                                         | Gingerol derivative | 1.34               | 1.68               | 1.78               |
| 27                                 | 27.37                   | 2291 | 2289        | 276                     | 137                | [6]-shogaol                                                                         | Gingerol derivative | 23.68              | 21.96              | 18.49              |
| 28                                 | 27.66                   | 2319 | ND          | 290                     | 151                | Me-[6]-shogaol                                                                      | Gingerol derivative | 0.61               | 0.71               | 0.38               |
| 29                                 | 27.76                   | 2328 | 2335        | 292                     | 137                | [6]-gingerdione                                                                     | Gingerol derivative | 1.90               | 1.57               | 2.56               |
| 30                                 | 28.38                   | 2387 | 2383        | 294                     | 137                | [6]-gingerol                                                                        | Gingerol derivative | 6.04               | 9.45               | 12.46              |
| 31                                 | 28.56                   | 2403 | ND          | 308                     | 151                | Me-[6]-gingerol                                                                     | Gingerol derivative | 0.44               | 0.48               | 0.65               |
| 32                                 | 28.97                   | 2449 | 2454        | 336                     | 137                | Acetoxy-[6]-gingerol                                                                | Gingerol derivative | 0.25               | 0.18               | 0.97               |
| 33                                 | 29.25                   | 2480 | ND          | 296                     | 137                | [6]-gingerdiol                                                                      | Gingerol derivative | 3.27               | 3.49               | 4.32               |
| 34                                 | 29.37                   | 2494 | 2489        | 338                     | 137                | Isomer of 5-acetoxy-[6]-gingerdiol                                                  | Gingerol derivative | 0.86               | 0.92               | 1.16               |
| 35                                 | 29.47                   | 2504 | 2506        | 380                     | 137                | Diacetoxy-[6]-gingerdiol                                                            | Gingerol derivative | 8.72               | 7.38               | 8.31               |
| 36                                 | 29.66                   | 2526 | 2524        | 394                     | 151                | Methyl diacetoxy-[6]-gingerdiol                                                     | Gingerol derivative | 1.35               | 1.40               | 2.01               |
| 37                                 | 29.80                   | 2541 | ND          | 320                     | 137                | [8]-gingerdione                                                                     | Gingerol derivative | 1.00               | 0.36               | 1.11               |
| 38                                 | 30.28                   | 2595 | 2592        | 290                     | 177                | 1-dehydro-[6]-gingerdione                                                           | Gingerol derivative | 2.56               | 1.66               | 3.34               |
| 39                                 | 31.28                   | 2717 | 2720        | 332                     | 137                | [10]-shogaol                                                                        | Gingerol derivative | 6.96               | 4.30               | 4.16               |
| 40                                 | 31.61                   | 2758 | 2762        | 348                     | 137                | [10]-gingerdione                                                                    | Gingerol derivative | 3.39               | 1.49               | 3.16               |
| 41                                 | 34.02                   | 3078 | 3077        | 430                     | 137                | [6]-gingerdiol (2E)-geranial acetal                                                 | Gingerol derivative | 1.67               | 2.64               | 2.80               |
| 42                                 | 34.53                   | 3146 | ND          | 356                     | 137                | Gingerenone A                                                                       | Gingerol derivative | 0.41               | 0.48               | 0.59               |
| <b>Sum of quantified volatiles</b> |                         |      |             |                         |                    |                                                                                     |                     | <b>84.34</b>       | <b>83.54</b>       | <b>83.59</b>       |

\*literature LRI values: Bartley and Jacobs (2000), El-Sayed (2021), Huang et al. (2012), Nishidono et al. (2020), Singh et al. (2008).

ND = no data available.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.crfs.2021.08.010>.

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