

## Aqueous Extract Composition of Spent Ginger (*Zingiber officinale* var. *Amarum*) from Essential Oil Distillation

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**Abstract.** Ginger (*Zingiber officinale* var *Amarum*) is widely used as raw material for essential oil production in Indonesia and contain high functional compounds. After producing essential oil, distillation leave less valuable spent ginger. This research was conducted to determine the bioactive compounds remained in aqueous extract of the spent ginger. The extracts were produced at various combination of temperature (55, 75, 95°C) and duration (15, 30, 45 minutes). The extract composition was observed using Gas Chromatography - Mass Spectrometry analysis. The temperature and time of maceration extraction affected the content of compounds in spent ginger aqueous extracts. The extracts contained four largest components of  $\alpha$ -curcumene,  $\alpha$ -zingiberene,  $\beta$ -sesquiphellandrene and  $\beta$ -bisabolene. The aqueous extracts from spent ginger contained the compounds which may contribute to distinctive flavor of ginger and also bioactive function.

### 1. Introduction

Ginger rhizome is widely used as a kitchen spice or medicine around the world. It has a distinctive spicy flavor and a pleasant aroma so that since many centuries, it has been extracted by boiling in water for beverage. The Koran, as moslem scripture, mentions (chapter 76/ Al-Insaan, verse 17) that the drink of "zanjabil" (which is an Arabic word for ginger) is served to the inhabitants of heaven. Among other varieties, in Indonesia, *Zingiber officinale* var *Amarum* is the most popular spice used by people to cook and produce essential oils, because although it has small rhizome size, but has soft fiber, and strong aroma. Its aroma is not too spicy like red ginger. Ginger contain zingerone, shogaol, gingerol, paradol,  $\beta$ -phellandrene, curcumene, cineol, geranyl acetate, terpeneol, terpene, borneol, geranyl, limonene, zingiberol, linalool,  $\alpha$ -zingiberene,  $\beta$ -sesquiphellandrene,  $\beta$ -bisabolene, zingiberenol and  $\alpha$ -farnesene [1].

Ginger compounds act as antioxidants which are phenolic compounds (such as 6-gingerol and 6-shogaol), alanine, and vitamin C. Antioxidant compounds have an important role in the human health and are also widely used as food additives to prevent food damage [2, 3].

High value commodity from ginger processing is essential oil produced by distillation. The ginger oil industries also produce spent ginger as by product. Generally, these by products are dried and directly used as boiler fuel of distillation, whereas the bioactive compounds allegedly remain in the spent ginger.

The extraction of the bioactive compounds from spent ginger using organic solvent is the most popular method recently. However, concern about food safety related with solvent residue remaining in the extract probably limit consumer acceptance when the extract applied into food processing. The



use of ethanol as a solvent in the extraction for food purposes also rises doubtness of halal state among Moslem consumer. Water is the cheapest solvent available, neutral, and harmless so it is safe when used in food manufacturing without any negative concern about remaining solvent, but its higher boiling point than the other solvent result in longer evaporation to concentrate the extract.

Time and temperature affect extraction rate. The longer time of extraction, the bigger chance of contact between solute and solvent, thus the more solute were extracted. Maceration provide a simple method of extraction, but it takes a longer time when the processing was held at room temperature. In order to accelerate the extraction, modifications in the method by using heating and stirring are effective. Increasing extraction temperature is very effective in accelerating the extraction process because the temperature exhibit mobility of solvent molecules and also cause pores of the solid raw material getting bigger. However some functional compounds of ginger are sensitive to the temperature fluctuation. Gingerol is converted into shogaol when ginger or its derivatives is heated with very high temperature. Therefore, the extraction temperature should be employed carefully to keep the important functional components in the extract.

Previous research concluded that highest total phenol and antioxidant activity in the extract was produced by brewing ginger powder (from fresh ginger/ not spent ginger) in water at 56.12°C [4]. Research on extraction of spent ginger from essential oil distillation using water has never been done. Furthermore, variations in temperature and extraction time probably affect the composition of spent ginger extract obtained. It is therefore necessary to study the effect of temperature and time of the spent ginger on the composition of the extract by the mean of Gas Chromatography - Mass Spectrometry (GC-MS) analysis. The GC-MS analysis had been used to determine components in air dried ginger root extract by other researchers [5]. The benefit of this study is to find a method for producing aqueous flavor extract from the spent ginger based on evaluation of components observed in the extracts.

## 2. Experimental

### 2.1. Materials.

Fresh ginger (*Zingiber officinale* var. *Amarum*) rhizome harvested after two years cultivation in December from Ngunut Village, Jumantono, Karanganyar, Central Java, Indonesia.

### 2.2. Methods

**2.2.1. Ginger oil distillation.** The ginger rhizome were sorted then washed and brushed to release soil and other impurities attached to its surface. Clean fresh ginger rhizomes were chopped using a knife by cutting cross with a thickness of  $\pm 0.6$  cm. Furthermore, the rhizomes were air dried until its visual appearance is wilted and not easily broken (moisture content  $23.08 \pm 0.21\%$ ). Essential oil distillation of ginger rhizomes was conducted in CV. Orizho, Bantul, Yogyakarta, Indonesia using steam distillation method. The distillation lasted for  $9 \pm 0.25$  hours until produced ginger essential oil and spent ginger as the by product.

**2.2.2. Spent ginger extraction.** The spent ginger rhizomes were then dried using a cabinet dryer at a temperature of 50-60°C for 27 hours until the water content is 5-7%. Dried spent ginger were grinded using a disk mill, then sifted (40 mesh). Furthermore, the spent ginger powder was extracted by maceration using distilled water as a solvent (the powder to the water ratio was 1: 5). The extraction the was performed at various temperature (55°C, 75°C and 95°C) which were combined with various extraction time (15 minutes, 30 minutes and 45 minutes). Furthermore, filtration using filter paper was conducted to separate filtrate / extract from the solid waste. Before tested, the spent ginger extracts were stored in dark amber bottles at 10°C.

**2.2.3. GC MS analysis.** The component identification was carried out using GC - MS equipped with mass Restek RxiTM-1ms column (30 m length). Helium was used as carrier gas at a constant flow of 0.44 ml/min in and an injection volume of 1  $\mu$ l was employed, injector temperature 280 °C; ion - source temperature 250 °C. The oven temperature was programmed from 100°C for 4 min, with an increase of 5°C/min, to 250°C. Total GC running time was 34 min.

### 3. Result and Discussion

**Table 1.** Composition of spent ginger aqueous extract (in relative percentage for each compound)

| Components                  | Extraction condition |       |      |      |      |       |       |       |      |
|-----------------------------|----------------------|-------|------|------|------|-------|-------|-------|------|
|                             | 55°C                 |       |      | 75°C |      |       | 95°C  |       |      |
|                             | 15'                  | 30'   | 45'  | 15'  | 30'  | 45'   | 15'   | 30'   | 45'  |
| Decanol                     | 0.93                 | -     | -    | -    | -    | -     | -     | -     | -    |
| $\alpha$ -zingiberene       | 0.99                 | 9.92  | -    | -    | 5.65 | 10.80 | 10.07 | 9.19  | -    |
| $\beta$ -sesquiphellandrene | 0.73                 | 12.44 | -    | -    | 4.43 | 11.32 | 10.81 | 10.98 | 4.95 |
| Nerolidol                   | 10.07                | -     | -    | -    | -    | -     | -     | -     | -    |
| 1-buthyl 2-octyl phthalate  | 0.89                 | -     | -    | -    | -    | -     | -     | -     | -    |
| Geranyl acetate             | 0.74                 | -     | -    | -    | -    | -     | -     | -     | -    |
| Phenol,4-ethyl-2-methoxy    | 0.73                 | -     | -    | -    | -    | -     | -     | -     | -    |
| Oxiranemethanol             | -                    | 1.77  | -    | -    | 7.95 | -     | -     | 2.42  | -    |
| Borneol                     | -                    | 3.18  | -    | -    | -    | -     | -     | -     | -    |
| $\alpha$ -curcumene         | -                    | 12.16 | -    | -    | 5.92 | 13.28 | 12.80 | 9.43  | 7.61 |
| Germacrene D                | -                    | 4.05  | 5.89 | -    | -    | -     | -     | -     | -    |
| $\beta$ -bisabolene         | -                    | 8.12  | -    | -    | 5.23 | 7.35  | 7.02  | 7.03  | -    |
| Furazan                     | -                    | -     | 6.44 | -    | -    | -     | -     | -     | -    |
| 2-camphonone                | -                    | -     | -    | -    | 5.54 | -     | -     | -     | -    |
| $\gamma$ -muurolene         | -                    | -     | -    | -    | -    | 2.89  | -     | -     | -    |

The  $\alpha$ -zingiberene,  $\beta$ -sesquiphellandrene,  $\alpha$ -curcumene, and  $\beta$ -bisabolene performed similarity index  $\geq 90$  in comparison with the library of mass spectra, while the others ranged 80-89.

Based on the result, the extraction should not be carried out at 55°C – 45 minutes, 75°C – 15 minutes, or 95°C – 45 minutes due to lack of functional or flavoring compounds (see table 1). At 55°C – 45 minutes or 75°C – 15 minutes, ginger starches might started to swell before they were gelatinized finally. The swelling starches probably absorbed most of the compounds, while the earlier gelatinized form of starches obstructed the constituents to be extracted by the water. Previous research observed the gelatinization temperature of ginger starch at  $78 \pm 0.1^\circ\text{C}$  [6]. At 95°C – 45 minutes, the aqueous spent ginger extract demonstrated only two detected compounds ( $\alpha$ -curcumene and  $\beta$ -sesquiphellandrene) but in low percentage. The longest extraction at high temperature (95°C) seemed to degrade most of the functional compounds.

The  $\alpha$ -zingiberene,  $\beta$ -sesquiphellandrene,  $\alpha$ -curcumene, and  $\beta$ -bisabolene were most frequently found in most of the extracts (see table 1). Those four compounds are sesquiterpenes commonly found in ginger essential oil, methanolic extract of ground ginger and also aqueous extract of roasted/boiled ginger [7, 8, 9, 10]. At longer extraction, the compounds performed a tendency of percentage increase, but  $\alpha$ -zingiberene,  $\beta$ -sesquiphellandrene and  $\alpha$ -curcumene decreased as the longer extractions were carried out at 95°C. Each compounds perform unique odor as follows:  $\alpha$ -zingiberene (warm-spicy,

weak woody),  $\beta$ -sesquiphellandrene (spicy, mild),  $\alpha$ -curcumene (spicy, herbal), and  $\beta$ -bisabolene (warm, spicy, sweet-balsamic) [5].

Nerolidol and borneol (see table 1) were also reported in research on ginger extracted by boiling ginger rhizome in water at 100°C [10]. It should be noted that nerolidol, which perform many bioactive function, were present in high percentage as the result of 55°C - 15 minutes extraction, but not found in other extracts. Borneol is monoterpene contributed to camphoraceous, peppery, and earthy odor [5]. Borneol compound was present in the extract from 55°C - 30 minutes treatment, while geranyl acetate was only present in the extracts of 55°C - 15 minutes treatment. The germacrene D, which contributed to dry-spicy and weak woody odor, was also found in the study of ginger powder extracted using a high pressure CO<sub>2</sub> at 12-14°C and 4.6-5.0 bar for 120 minutes [5]. The germacrene is sesquiterpene compound [11] but not all extracts contained this compound. The germacrene D was present in the result of 55°C - 30 minutes extraction and also 55°C - 30 minutes extraction.

Other compound found in the extract was phenol, 4-ethyl-2-methoxy (see table 1). This was also detected on the maceration extract of ginger powder at 50°C for 6 hours with ethanol solvent [12]. Camphonone was known as ginger extract component giving fresh and camphoraceous odor [5].

The key nonvolatile constituents in ginger are gingerol and zingerone [13]. However, the compounds were not found from the GC-MS analysis result (see table 1). This was probably due to degradation of the compounds as the result of high temperature employed during distillation. Phenolic compounds are sensitive, unstable and highly susceptible to degradation. The most important cause for phenolic degradation is the temperature [14]. In addition, drying of wet spent ginger probably affect gingerol compounds. The drying during material preparation also lower gingerol and increase terpene hydrocarbons in ginger rhizome [15].

Ginger rhizome contains compounds that act as antioxidants, including terpenoids and polyphenols [16]. Terpenoid is a type of compound derived from a combination of two or more units of isoprene. The terpenoids include monoterpenes, sesquiterpenes, terpenes, triterpenes, tetraterpenes and polymeric terpenoids. Sesquiterpenes are terpenoids that have 15 carbon atoms and composed of 3 isopropen units. Some of the aqueous spent ginger compounds, i.e. nerolidol (see table 1) belonging to sesquiterpenes which are medically important as bioactive compounds and perform antioxidant activity [17].

Based on each composition, the extract obtained at 75°C – 45 minutes, 95°C – 15 minutes or 95°C – 30 minutes indicated strong ginger flavor, while at 75°C – 30 minutes indicated mild ginger flavour with nuances in fresh and camphoraceous odor. The extract obtained at 55°C – 30 minutes indicated not only strong ginger flavour but also nuances in camphoraceous, peppery and earthy odor. All extracts mentioned above denoted same characteristic: warm, spicy, woody, herbal, sweet balsamic.

#### 4. Conclusion

The temperature and time of maceration extraction affected the content of compounds in spent ginger aqueous extract. The spent ginger aqueous extracts contained four largest components of  $\alpha$ -curcumene,  $\alpha$ -zingiberene,  $\beta$ -sesquiphellandrene and  $\beta$ -bisabolene. The aqueous extract from spent ginger contained compounds which contribute to distinctive flavor of ginger. Although GC-MS analysis revealed many key compounds, the using of more sensitive equipment such as High Performance Liquid Chromatography (HPLC) was suggested to cope with the absence of gingerol and shogaol as important flavoring agents and antioxidant compounds in the extract.

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## References

- [1] Obeten K E, Patrick O E, Victoria N I and Patricia P O 2015 *International Journal of Medical and Health Sciences Research* **2** 25-35
- [2] Tsai T H, Tsai P J and Ho S C 2005 *J. Food Sci.* **70** C93-7
- [3] Suhaj M 2006 *Journal of Food Composition and Analysis* **19** 531-37
- [4] Kishk Y F M and Hemat E E S 2010 *World Journal of Dairy and Food Sciences* **5** 188-96
- [5] Stoyanova A, Denkova Z, Nenov N, Slavchev A, Jirovetz L, Buchbauer G, Lien H N, Schmidt E and Geissler M 2006 *Electronic Journal of Environmental, Agricultural and Food Chemistry* **5** 1615-23
- [6] Kolawole A A, Igwemmar N C and Bello H A 2013 *International Journal of Science and Research* **2** 71-75
- [7] Kamaliroosta Z, Kamaliroosta L and Elhamirad A H 2013 *Journal of Food Biosciences and Technology* **3** 73-80
- [8] Buang F Jantan I Zawani Amran A Z and Arbain D 2014 *Research Journal of Applied Sciences, Engineering and Technology* **7** 5098-105
- [9] Hasan HA, Rasheed Raauf AM, Abd Razik BM and Rasool Hassan BA 2012 *Pharmaceut Anal. Acta* **3** 1-5
- [10] Purnomo H Jaya F and Widjanarko S B 2010 *International Food Research Journal* **17** 335-47
- [11] Suresh V N, Venugopalan V V, Joy B, Sreekumar M and Menon A N 2012 *Asian Pacific Journal of Tropical Biomedicine* **2** S1347-50
- [12] Jayanudin, Rochmadi, Wiratni, Yulvianti M, Barleany D R, and Ernayati W 2013 *Proceeding of International Conference on Chemical Engineering* Parahyangan University pp: 72-7
- [13] Zick S M, Ruffin M T, Djuric Z, Normolle D and Brenner D E 2010 *International Journal of Biomedical Science* **6** 233-40
- [14] Vatai T Skerget M and Knez Z 2009 *Journal of Food Engineering* **90** 246-54
- [15] Bartley J P and Jacobs A L 2000 *Journal of the Science of Food and Agriculture* **80** 209-15
- [16] Ghasemzadeh A Jaafar H Z E and Rahmat A 2011 *Journal of Medicinal Plants Research* **5** 1147-54
- [17] Chan W K, Tan L T H, Chan K G, Lee L H and Goh B H 2016 *Molecules* **21** 529