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Original Research Article

Extraction and Characterization of Essential Oil and Oleoresin from Ginger Rhizome using Near-Critical Condition in a Modified Autoclave

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ABSTRACT

Ginger (Zingiber officinale Roscoe) is an important and widely used spice for both culinary and medicinal purposes for more than 3500 years. The study is aimed at extraction and analysis of the essential oil from fresh and dried ginger rhizome. The oils were obtained by near-critical conditions in a modified high-pressure fluid extraction unit using liquid carbon dioxide and analysed using Fourier Transform Infrared Spectroscopy (FT-IR), Gas Chromatography Mass Spectrometry (GC-MS) and High-Performance Liquid Chromatography (HPLC). A maximum of 2.3% was obtained from the dried ginger while the fresh ginger contained 1.0% indicating that the dried ginger yields more oil than the fresh ginger. The following compounds: hydroxyl, alkanes, carboxylic acid, carbonate-carboxylic, amines, aldehydes, alcohol and carbonyl functional groups were revealed in the FT-IR analysis. Analysis of GC-MS and HPLC-MS identified seven and eight components, respectively. The major qualitative and quantitative constituents in the fresh and dried extracts of the Nigerian ginger essential oil using liquid carbon dioxide for extractions are gingerol (21.36%, 20.36%), followed by zingerone (10.86%, 10.86%), zingiberene (10.12%, 10.12%), shogaol (6.15%, 4.83%), paradol (6.11%, 6.42%), α-farnesene (3.26%, 4.97%) and piperine (4.01%, 4.01%) using GC-MS. While HPLC-MS analysis gives shogaol (24.65%, 25.96%), followed by gingerol (18.52%, 20.04%), 8-gingerol (8.31%, 14.01%), paradol (11.58%, 10.48%), vanillic acid (6.95%, 3.03%), (10)-shogaol (5.47%, 6.86%), zingerone (5.74%, 3.72%) and [8]-dehydrogingerdione (5.72%, 4.16%). In conclusion, it therefore shows that the dry ginger gives higher yield than the fresh ginger likewise bioactive compounds were identified and quantified in the fresh and dried gingers.

1. INTRODUCTION

Herbs and spices of which ginger rhizome is grown in many countries such as India, China, Nigeria, Australia and Jamaica (Bartley and Jacobs, 2000). It is an herbaceous perennial plant with a wide range of uses as a spice and grown in many tropical and subtropical areas of the world (Pradeep *et al*., 2016). It belongs to the

Zingiberaceae family and has the botanical name *Zingiber officinale* Roscoe (Abdo *et al*., 2018; Kamal *et al*., 2023).

Ginger rhizome (*Zingiber officinale* Roscoe) is a valuable source of food, income and healthcare, forming the basis of medicinal therapy prior to the development of synthetic drugs. Ginger products are constituents of many pharmaceutical preparations (Norsyamimi *et al*., 2020) and besides their culinary value, there is an increased interest in using ginger and other natural products in clinical pharmacology research in the treatment and prevention of various diseases (Mahboubi, 2019; Jones, 2007). Ginger has a high commercial value in the local and international markets and they play a crucial role in enhancing the flavour, colour, aroma of food, and beverages in the human diet (Smith & Johnson, 2021). They are often preferred over synthetic drugs because of their minimal side effects (Mudgil & Barak, 2017).

Traditionally, ginger rhizomes have been widely employed in various traditional systems of medicine around the world including Traditional Chinese Medicine, Ayurvedic, Tibb-Unani herbal medicine (Yasmin *et al*., 2022) and traditional healers and medicine practitioners of Nigeria and is being studied for its potential uses in modern medicine resulting in a significant market demand for herbal medicines (Ramakkrishna *et* al., 2016; Mudgil & Barak, 2017). There is a growing demand for essential oils and oleoresins produced from ginger and there is the need for research on its value-added products on the best way to extract these substances that will identify an optimum extraction technique that will ensure high yields and quality.

The chemical composition of these products varies which is the essence of this study is influenced by many factors depending on the geographical origin, extraction techniques, raw materials (freshness or dryness of rhizomes), extraction solvents used and its preparation (Sejali & Anuar, 2011). Ginger products are generally consumed or utilized as fresh green ginger, dried ginger, sliced preserved ginger, powdered ginger, as well as essential oil and oleoresin extracted from ginger rhizome (Vasala, 2012; Lobo *et al*., 2021; USDA, 2021; WHO, 2021).

Essential oils can be defined as a highly concentrated, hydrophobic (insoluble in water), and lipophilic (soluble in organic solvents) liquids rich in volatile aromatic compounds, giving plants their unique scents, flavours, and essence (Kumar *et al*., 2021). Oleoresins on the other hand, represent a concentrated liquid extracts of spices that contain both volatile oils and non-volatile resins obtained through extraction with a non-aqueous solvent, followed by solvent removal through evaporation (Gupta *et al*., 2022).

Ginger has also been shown to have benefits due to essential oil and oleoresin content which work as an antioxidant to stabilize or neutralize free radicals (ROS) that cause muscle damage and pain (Chiang *et al*., 2009), boost the immune system, protects the body from invading pathogens like viruses and bacteria, identify and destroy cancer cells that appear in the body, and clean old cells and damaged tissue (Sherwood, 2013), therefore Food and Drug Administration (FDA) has classified ginger as generally recognized as safe (GRAS) (Rayati *et al*., 2017). Ginger has anti-inflammatory properties due to the presence of phenolic compounds in ginger that play a role in eliminating free radicals (Indiarto *et al*., 2019) and reduce nausea (vomiting) in pregnant women (Anita, *et al*., 2020). An important source of natural flavour and its preservative properties of ginger makes it useful in variety of food products which includes baked goods (ginger bread and biscuits), candy, confectionery, meat, and soft drinks (Brown *et al*., 2021; Smith and Davis, 2022; Shaukat *et al.,* 2023).

Ginger has a long history of use in traditional medicine practice for the treatment of various conditions such as gastrointestinal disorders (Ghayur and Gilani, 2005), rheumatological diseases such as arthritis, digestive disorders and pain (Ramadan *et al*., 2011; Ramadan and El-Menshawy, 2013; Walstab *et al*., 2013; Funk *et al*., 2016; Nikkah *et al*., 2019). Modern research has shown that ginger has antioxidant, anti-cancer (Wang *et al*., 2015; Zick *et al*., 2015), may also help in the prevention of chemotherapy-induced toxicity (Marx *et* al., 2017), improve inflammatory bowel disease and colitis (Zhang *et al*., 2018) and anti-inflammatory properties (Mao *et al*., 2019).

The fragrance compounds found in ginger essential oil and oleoresin are also used in the petroleum industry to make solvents and lubricating oils and in the pharmaceutical industry for antiseptics and aromatherapy products (Edris, 2007). They are often used in the perfume and cosmetic industries, as well as in deodorants,

soaps, detergents, and various industrial products like animal feeds, paints, and insecticides (Black, 2021; Johnson and White, 2023).

There are two main methods of extraction: traditional and modern. Traditional methods include hydro-distillation, steam distillation, organic solvent extraction, effleurage, maceration, and cold pressing. These methods have certain drawbacks (Gavahian *et al*., 2012), and these drawbacks have spurred researchers to develop newer, more advanced methods like near-critical liquid carbon dioxide ($NCLCO_2$) (Smith *et al*., 2021) and supercritical fluid extraction (SFE), ultrasound-assisted extraction (UAE), microwave-assisted extraction (MAE) and pressurized fluid or liquid extraction (PFE or PLE) (Majid *et al*., 2023) with carbon dioxide being the most favoured solvent. These modern methods have advantages like improved efficiency and yield, reduced solvent usage and faster extraction times. This method will prevent the thermal degradation of gingerols that occurs at higher temperatures.

Gingerols found in ginger are thermally unstable when heated due to their β-hydroxy keto group in the structure and are prone to two primary chemical reactions (Siyaftri *et al*, 2018) during preparation of extracts and storage (Madonna and Wilfred, 2022). The first reaction involves the dehydration of the hydroxyl ketone grouping and the second reaction which is the retro-aldol reaction of the hydroxyl ketone grouping. These reactions can produce shogaols, zingerone and a series of aliphatic aldehydes under high temperature (Mahboubi, 2019). Paradol, akin to gingerol, is produced upon the hydrogenation of shogaol. Therefore, this study is aimed at extraction and characterization of essential oil and oleoresin from ginger rhizome near-critical conditions using a modified high-pressure fluid extraction (HPFE) unit.

2. MATERIALS AND METHODS

2.1. Material Collection and Preparation of Samples

Fresh ginger rhizomes (5 kg) were purchased from the local market in Kaduna state, Nigeria. The ginger was prepared for extraction by properly washing it with tap water to remove any adhering dirt, stone and extraneous material and then divided into two parts. One part was stored in a freezer to maintain the quality of the chemical compounds while the other part was sliced into 2-3 mm thick pieces air dried in an oven at 40 °C until the moisture content was approximately 10-12%. The dried ginger was ground to a 250 and 500 µm particle sizes and stored in airtight black plastic bags to prevent microbial growth and biochemical reactions until they were needed for experiments (Taylor and Brown, 2022). All chemicals and reagents used in this work are of analytical grade.

2.2. Extraction of Active Constituents of Ginger Rhizome

Figure 1 shows the schematic process flow diagram of a customized Jennings's type autoclave (Jennings *et al*., 1981) used in the extraction of ginger essential oil $NCLCO_2$ condition. All the valves on the equipment including those on CO_2 cylinder tank were initially closed. A 1:20 g/g of the sample to solvent ratio was used and approximately 10 g of the sliced 2 mm fresh sample or 5 g of the ground dried sample were each weighed and loaded separately on either a perforated mesh or in a glass thimble with filter, placed on a tripod stand and the extractor chamber was placed on a weighing balance to measure the required amount of solvent. Then, the valve on the liquid CO_2 tank was fully opened while the regulatory and delivery valves were partially opened so as to meet the capacity of the chiller being able to chill the CO_2. The solvent inlet valve was opened to allow the flow of CO_2 to pass through the CO_2 purifier and a condenser attached to a chiller into the extractor chamber in order to measure the precise amount of CO_2 as shown in Figure 1. The extractor chamber was inserted into the thermostatic electrothermal heating chamber, the heater control knob was switched on, and temperature through the system was regulated by the chiller and the heater temperature tuned to the pre-set value of 28ºC on the digital electronic indicator for the time duration of 90 minutes. At the end of the time, the solvent recovery outlet control valve was opened to separate the solvent from the extract via a separating funnel leaving behind the extract in the extractor chamber. After the separation, the extract was filtered, extraction yield determined after drying the residue and refrigerated until required for analysis. The Percentage yield of the extract was calculated using Equation (1)

$$\% Y = \frac{M_i - M_f}{M_i} x\ 100 \quad (1)$$

Where Y is the percentage extraction yield, M_i is the initial mass of the sample in g and M_f is the final mass of sample after extraction in g

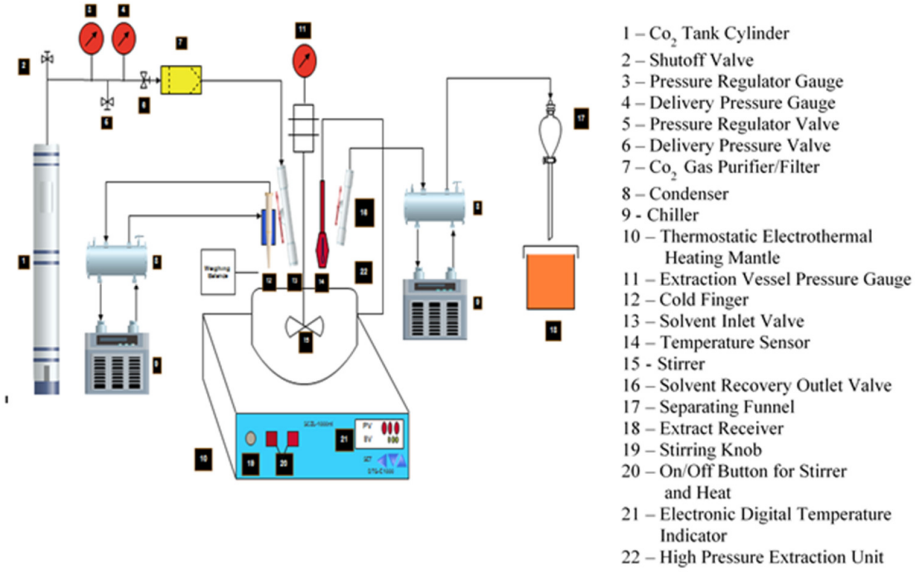


Figure 1: Complete schematic process flow diagram of the modified high-pressure fluid extraction (HPFE) unit (Mohammed, 2020)

2.3. Characterization

The analysis of the active constituents of fresh and dried ginger was carried out by the use of FT-IR, GC-MS and HPLC-MS.

2.3.1. Fourier transform-infrared spectroscopy (FT-IR) Analysis

FT-IR spectroscopy usually requires sample preparation before analysis. The sample was mixed with a solvent commonly potassium bromide with a mixing ratio of 1 to 100. Then, the mixed powder is pressed in a die at a load of 10 tons to form a pellet of 13 mm. The pellet was then inserted in the FT-IR chamber for analysis. The pellet was washed three times with 10 ml of de-ionized water to get rid of the free proteins/enzymes that are not capping the samples. The samples were dried and ground with potassium bromide (KBr) pellets and analysed. Also, it acts as a carrier for the infrared spectrum. Furthermore, the reference material of potassium bromide will be used to plot the transmittance. The FT-IR analysis was conducted to detect the changes in the functional groups of the raw and carbonized sample. Sample tablets were prepared by mixing each sample with potassium bromide (the ratio of sample to KBr was 1:100) before analysis. The spectra were recorded within the frequency range of 4000 cm^{-1} to 500 cm^{-1} using an FT-IR spectrometer (Infrared spectrometer Varian 660 MidIR Dual MCT/DTGS Bundle with ATR)) with a detector at 4 cm^{-1} resolution and 200 scans per sample. The refractogram obtained from FT-IR spectroscopy between wave number and absorption was tabulated and Infra-red solution software was employed for getting the spectrum (ABUAD, 2024).

2.3.2. Gas chromatography-mass spectrometry sample analysis

Before proceeding to the GC-MS analyses, 2 mg of perdeuterated benzene in methanol were added as internal standard (I.S.) in all the samples. The chemical composition of ginger essential oil was analysed by a gas chromatograph coupled with a mass spectrometer detector was performed using Varian 3800/4000 gas

chromatograph mass spectrometer equipped with an Agilent mass selective detector, equipped with a silica capillary column (30 x 0.25 mm ID x 0.25 µm film thickness, 5% Phenyl, 95% Dimethyl Polysiloxane (Agilent Technologies, Santa Clara, CA, USA). Nitrogen was used as the gas carrier at flow rate of 1 µL of the injected volume was measured by PTV injector operating in splitless mode (SL time 0.6 min). The GC injection temperature was set at 200 °C for 0.05 min and at 14.5 °C s^{-1} up to 300 °C for 0.6 min. The temperature program starts at 2.0 mL min^{-1} and after 20 min at 1.1 mL min^{-1} rate, up to 3.5 mL min^{-1} for 25 min. The optimized chromatographic run is 50 °C (hold time 1 min), ramp 7 °C min^{-1}, 100 °C (0 min), ramp 10 °C min^{-1}, 240 °C (30 min). The eluted analytes were detected using Mass Selective detector acquisition in scan mode (29–350 *m/z*) with 0.2 s scan time and emission current of 50 µA and an electron impact ionization energy of 70 eV in EI+ mode. The source temperature was set up at 260 °C and the transfer line temperature at 240 °C. Data acquisition, processing and handling are performed using ChemStation software. Identification of unknown compounds were done on the basis of gas chromatographic retention times with authentic compounds and the spectral data collected from NIST and Wiley Spectral library search programme. No response factors were calculated. All the samples and replicates were continuously injected as one batch in random order to discriminate technical from biological variations. Additionally, the prepared pooled samples were used as quality controls (QCs), which were injected at regular intervals throughout the analytical run to provide a set of data from which the repeatability can be assessed (ABUAD, 2024).

2.3.3. High performance liquid chromatography-mass spectrometry sample analysis

The chromatographic analyses of the ginger extracts obtained from optimum $NCLCO_2$ were performed on a Shimadzu model SCL-10AVP apparatus equipped with two LC-10AD analytical pumps connected to an SPD-M10AVP diode drag detector and an SIL-9A automatic injector controlled by a communication module SCL-10AVP. The analyses were performed on a Phenomenex reverse phase C-18 column (Luna C-18 150 × 4.6 mm, 5 µm), and the data were analyzed using the program Class-VP version 6.10 program. All samples were dissolved in methanol (HPLC grade) at a concentration of 1 mg/mL and filtered through a 0.45 µm filter (Acrodisc CRPTFE). Acetonitrile/water mobile phase (54:46), flow rate of 1 mL/min.; injection volume of 20 µL and wavelength of 660 nm were used. The extracts were analyzed by HPLCMS using a Shimadzu SPD-M10AVP diode array detector. The data were then analyzed using the program Class-VP version 6.10 and mass spectrometric analyses were performed on a Bruker, Esquire 2000 plus in positive electrospray mode, 4.5 kV capillary voltage and 40 eV in the skimmer (ABUAD, 2024).

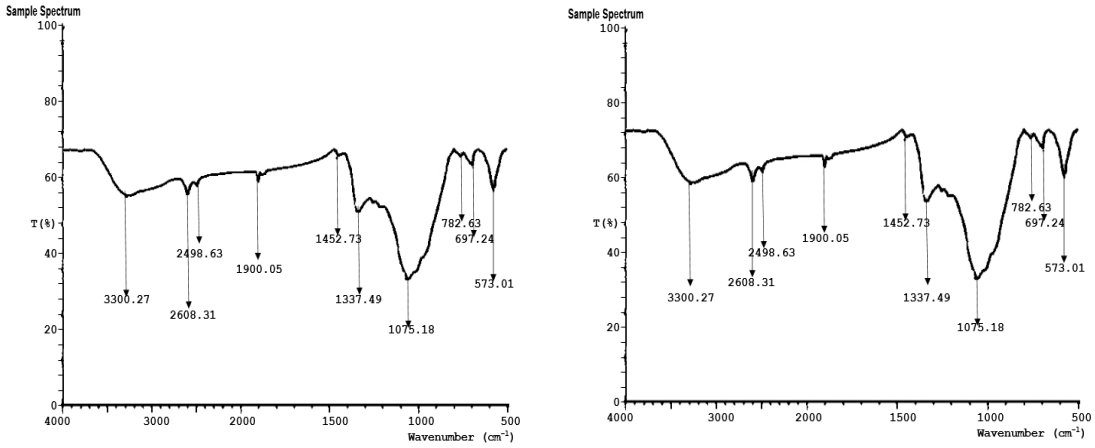
3. RESULTS AND DISCUSSION

3.1. Percentage Extract Yield of Ginger Essential Oil

The effects of extraction parameters such as sample-to-solvent ratio, extraction temperature, contact time and particle size on the yield of ginger essential oil were studied. These process parameters are the optimums from the preliminary investigations earlier carried out using $NCLCO_2$ extraction. The results of extraction of ginger essential oil content from the dried and fresh ginger samples showed that the dried ginger had a higher yield of 2.3% compared to fresh ginger which had a yield of 1.0%. This is in line with Shah and Garg (2014) who stated that the volatile oil content of African ginger varied between 0.8-4.2% on dry basis. This indicates that dried ginger has more oil than fresh ginger.

3.2. Identification of the Types of Chemical Bonds

The FT-IR analysis results of the extracted essential oil from the fresh and dried gingers were shown in Figures 2a and 2b. Several peaks were displayed and the identified peaks representing the functional groups were summarized in Table 1. The figures show the IR spectra of the essential oil with several peaks representing different functional groups. Table 1 shows the results of the peak assignment, including peak number, functional group and absorption bands of the extracts from fresh and dried ginger. Based on the results of the FT-IR analysis of the ginger extracts, several functional groups present include phenolic, aromatic, carboxylic acid, amines, alkanes, aldehydes and alcohols.



(a) (b)

Figure 2 (a & b): FT-IR spectrums of ginger essential oil of $NCLCO_2$ extractions of fresh and dried ginger

Table 1: Functional groups and compounds found in fresh and dried ginger samples $NCLCO_2$ extraction

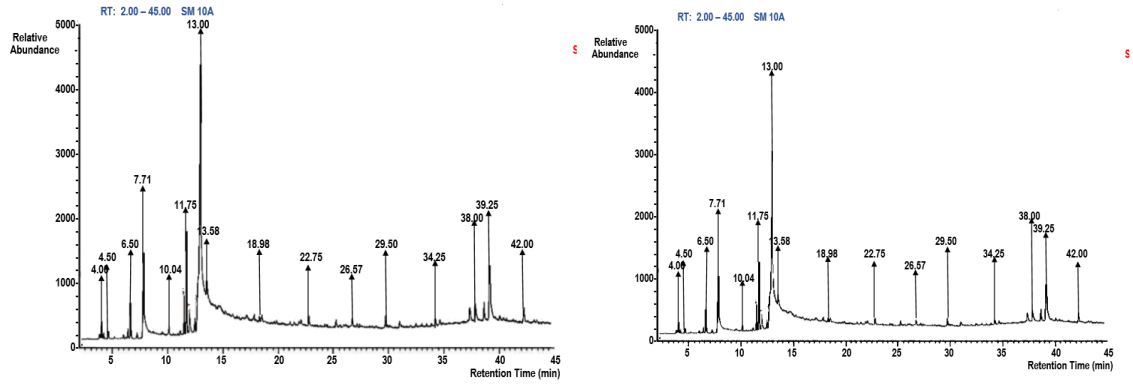
Sample Peak Run	Peak wavelength (cm^{-1})	Transmittance (%)	Assignment	Functional group samples in bracket
1	3300.27	56.98-60.13	O-H stretching vibration which corresponds to phenolic compounds	Hydroxyl group or phenol
2	2608.31	57.10-60.19	$-CH_3$ stretching vibration which corresponds to alkyl chains of phenols, and flavonoids.	Alkanes, methyl $-CH_3-$
3	2498.63	58.69-62.75	C=O stretching vibration	Carboxylic acid (Aromatic)
4	1900.05	60.15-64.38	C=O antisymmetric & carboxylic symmetric stretching acid vibration in carboxylate groups due to formation of carbonate	Carbonate-carboxylic group during pyrolysis
5	1452.73	65.23-69.43	C-H stretching vibration	Amines
6	1337.49	52.50-55.41	N-H bending in fatty amine or secondary amine C-H stretching vibrations corresponding to amines	Amines
7	1075.18	32.17-32.65	C-O stretching vibrations attributed to polysaccharides	Aldehydes
8	782.63-872.15	64.82-70.98	C-O-H stretching vibrations attributed to starch present in the sample	Alcohol (-CH2OH)
9	685.37-697.24	63.05-68.45	C=O stretching vibrations of β-ketones $N-H_2$ & N-H stretching vibration	Carbonyl (Aromatic) Amine
10	573.01	58.29-61.82	C-H stretching vibration	Alkanes

From the single bond range of 2500-4000 cm^{-1}, the wideband absorption observed in Figures 2a and 2b at 3300.27 cm^{-1} corresponds to the OH stretching vibration of primary alcohol or phenol that exists in both samples. There are no other peaks between 3000-3200 cm^{-1}, and the band observed at 2608.31 cm^{-1} shows that there is $-CH_3$ bond of alkane. Between 1900.05-2498.63 cm^{-1}, there exists C=O double bond and O-H

stretching vibration in H-bonded of carboxylic acid (RCOOH) and no peak was detected for a triple bond (C≡C) between 2000-2500 cm^{-1}. Likewise, the band observed at 1337.49-1452.73 cm^{-1} corresponds to C-H and N-H stretching and bending vibrations of amines. The band between 685.37-1075.18 cm^{-1} where a strong signal was detected shows the presence of carbonyl, alcohol and aldehyde compounds. All the bands almost agree with literature peak values reported by Ameh *et al.* (2020).

3.3. GC-MS Analysis of $NCLCO_2$ Extraction of Fresh and Dried Ginger

The chromatograms of fresh and dried ginger essential oil extracts are presented in Figures 3a and 3b while its identification and quantification from GC-MS analysis are shown in Table 2. The GC-MS analysis identified a total of sixteen compounds each in the ginger oil extracts of fresh and dried gingers. The GC-MS analysis has revealed the existence of eleven major bioactive chemical compounds in the essential oil extracts in comparison to the standard out of which zingiberene, α-farnesene, α-clovene, and trsnscubebol are sesquiterpene hydrocarbons while gingerol, shogaol and paradol are phenolic compounds while others are 4-isogingerol, γ-sitosterol and piperine $NCLCO_2$ extraction. The major qualitative and quantitative constituents in the fresh and dried extracts of the Nigerian ginger essential oil using liquid carbon dioxide as the solvent near critical conditions are gingerol (21.36%, 21.36%), followed by zingerone (10.86%, 10.86%), zingiberene (10.12%, 10.12%), α-clovene (6.97%, 3.65%), shogaol (6.15%, 4.83%), paradol (6.11%, 6.42%), α-farnesene (3.26%, 4.97%), transcubebol (4.14%, ND), γ-sitosterol (4.13%, 4.06%), piperine (4.01%, 4.01%) and 4-isogingerol (ND, 3.15%). From the above result, it shows that the percentage weight component of gingerol is more in fresh ginger than the dried ginger while zingerone, zingiberene and piperine have same amounts. Shogaol is higher in fresh ginger while paradol and α-farnesene are higher in the dried ginger. γ-sitosterol and α-clovene were found in both fresh and dried ginger while trans-cubebol was found in fresh ginger and 4-iso-gingerol was found in the dried ginger. α-farnesene and α-clovene for the fresh and dried ginger were detected on same retention times of 10.04 and 13.58 minutes, respectively while transcubebol was found at same retention time of 22.75 minutes for dried ginger and 4-isogingerol was not also found for the fresh ginger. In a similar manner, Hassan *et al.* (2012) identified seven major components in comparison with the standard. From the terpene family are mostly the sesquiterpene hydrocarbons among which are zingiberene (9%) and α-farnesene (11%), phenolic compounds which are gingerol (25%) and shogaol (18%) using methanol as a solvent in a soxhlet extraction apparatus. Hazim *et al* (2019) also reported the amount of zingiberene detected in the GC-MS analysis to be 10.86% which is in agreement when compared to the amount detected in this research work to be 10.12%. The paradol detected in this study was almost doubled (6.11%) when compared to the one reported by Hazim (3.97%) for fresh ginger using water distillation in a Clevenger apparatus. Siyaftri *et al* (2018) detected the amount of zingiberene (6.06%) and β-farnesene (3.57%) while in this study, the amount of zingiberene and α-farnesene are higher (10.12%, 4.97%), respectively.



(a) (b)

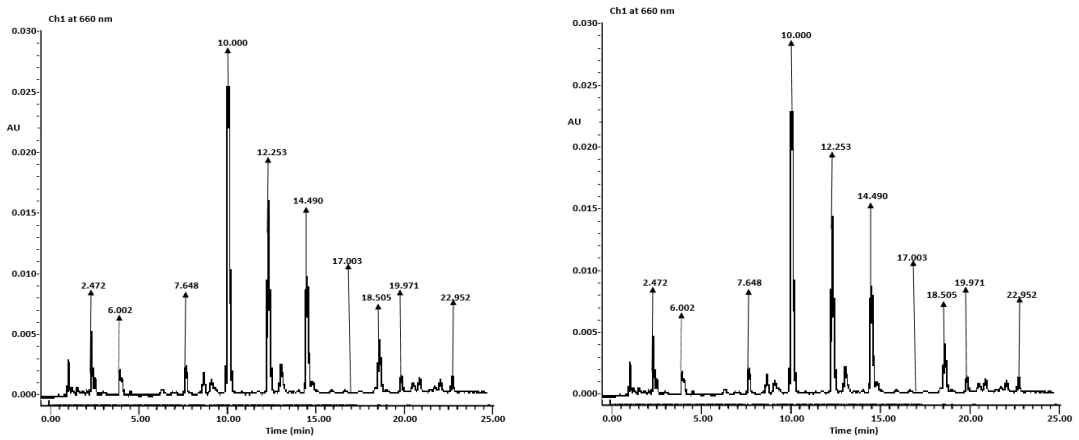
Figure 3 (a & b): GC-MS chromatograms of ginger essential oil of $NCLCO_2$ extractions of fresh and dried ginger

Table 2: GC-MS chemical constituents of ginger essential oil of $NCLCO_2$ of fresh and dried ginger

Peak No	RT (min)	Component detected	Molecular formula	Molecular weight	Component % weight CO_2FG	CO_2DG
4	7.71	1,3-Cyclohexadiene, 5-(1,5-dimethyl-4-hexenyl)-2-methyl-, [S-(R*,S*)]-(Zingiberene)	$C_{15}H_{24}$	204	10.12	10.12
5	10.04	α-Farnesene	$C_{15}H_{24}$	204	3.26	ND
		α-clovene	$C_{15}H_{24}$	204		3.65
6	11.75	Zingerone	$C_{11}H_{14}O_3$	194	10.86	10.86
7	13.00	Gingerol	$C_{17}H_{26}O_4$	294	21.36	20.36
8	13.58	α-Farnesene	$C_{15}H_{24}$	204	ND	4.97
		α-clovene	$C_{15}H_{24}$	204	6.97	ND
10	22.75	[4]-isogingerol	$C_{15}H_{22}O_4$	266	ND	3.15
13	34.25	Transcubebol	$C_{15}H_{26}O$	222	1.97	ND
		Piperine	$C_{17}H_{19}NO_3$	285	4.01	4.01
14	38.00	Shogaol	$C_{17}H_{24}O_3$	276	6.15	4.83
15	39.25	Paradol	$C_{17}H_{26}O_3$	278	6.11	6.42
16	42.00	γ-sitosterol	$C_{10}H_5Cl_9$	414	4.13	4.06

3.4. HPLC-MS Analysis of $NCLCO_2$ Extraction of Fresh and Dried Ginger

The chromatograms of fresh and dried ginger essential oil extracts are presented in Figures 4a and 4b while its identification and quantification from HPLC-MS analysis are shown in Table 3. The HPLC-MS analysis identified a total of 10 compounds each in the ginger oil extracts of fresh and dried gingers. The HPLC-MS analysis revealed the existence of ten major bioactive chemical compounds in the essential oil extracts of which shogaol, gingerol, and paradol are phenolic compounds and their series of homologous phenolic ketones series such as (8)-gingerol and (10)-shogaol, and its derivative [8]-dehdro-gingerdione. Others are oxalic acid and vanillic acid. Gingerol through retro-aldol reaction can lead to the production of zingerone and series of aliphatic aldehydes. The major qualitative and quantitative constituents in the fresh and dried extracts of the Nigerian ginger essential oil using liquid carbon dioxide as the solvent near critical conditions are shogaol (24.65%, 25.96%), followed by gingerol (18.52%, 20.04%), 8-gingerol (8.31%, 14.01%), paradol (11.58%, 10.48%), vanillic acid (6.95%, 3.03%), (10)-shogaol (5.47%, 6.86%), zingerone (5.74%, 3.72%) and [8]-dehydrogingerdione (5.72%, 4.16%). In comparison to Wohlmuth *et al.* (2005) where only 6-gingerol was identified as the major component, 8- and 10- gingerols were in lower percentage weight, while this study had 6-gingerol, 8-gingerol and paradol as the major phenolic compounds in the samples, and 10-shogaol and zingerone occurred in lower concentrations as identified by HPLC.



(a) (b)

Figure 4 (a & b): HPLC-MS chromatograms of ginger essential oil of NCLCO2 extractions of fresh and dried ginger

Table 3: Target components detected in liquid carbon dioxide of fresh and dried ginger extracts by HPLC analysis

Peak no	RT (min)	Component detected	Molecular formula	Molecular weight	Component % weight CO_2FG	CO_2DG
2	6.002	Zingerone	$C_{11}H_{14}O_3$	194	5.74	3.72
4	10.000	Shogaol	$C_{17}H_{24}O_3$	276	24.65	25.96
5	12.253	Paradol	$C_{17}H_{26}O_3$	278	11.58	10.48
8	18.505	8-Gingerol	$C_{19}H_{30}O_4$	322	8.31	14.01
9	19.971	Gingerol	$C_{17}H_{26}O_4$	294	18.52	20.04
10	22.971	(10)-Shogaol	$C_{21}H_{32}O_3$	332	5.47	6.86

4. CONCLUSION

The extraction process parameters produced a pale-yellow colour of ginger essential oil extract of 2.3% from dried ginger rhizome as against 1.0% of fresh ginger which is in line with Shah and Garg, (2014) that yield varies between 0.8-4.2% surpassing the performance of most extraction alternatives. The results of this research work has therefore shown that sample-to-solvent ratio, extraction temperature and extraction time near-critical liquid carbon dioxide extraction in a modified high pressure fluid extraction unit played an important role on the extraction of bioactive compounds. Identification some of important bioactive compounds using GC-MS technique were successful in this study. Both fresh and dried ginger contained gingerol, zingerone and zingiberene in the GC-MS analysis in same component % weight while shogaol, gingerol and (8)-gingerol are in different component % weight. The percentage weights of fresh and dried gingers are much higher when compared to Hassan *et al.* (2012). The major qualitative and quantitative constituents in the fresh and dried extracts of the Nigerian ginger essential oil using liquid carbon dioxide as the solvent near critical conditions are vanillic acid, zingerone and [8]-dehydrogingerdione while the main pungent compounds are a series of homologous compounds are shogaol, gingerol, 8-gingerol, paradol and (10)-shogaol are reported to possess anti-inflammatory, antioxidants and anticancer activities by Anisa *et al.* (2014) and Sultana and Ali. (2015).

5. ACKNOWLEDGMENT

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6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

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