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Pelagia Research Library

Der Chemica Sinica, 2014, 5(1):128-134

Pelagia Research Library

ISSN: 0976-8505
CODEN (USA) CSHIA5

Chemical analysis of locally cultivated garlic and it's oil

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ABSTRACT

This research work examines the chemical composition of Garlic cultivated in Sokoto Northwestern Nigeria using AAS analysis. It contains P, Mn and Cu (0.013) (0.0024) and (0.0012) respectively. This made Garlic a very valuable source of minerals. The results obtained indicates that garlic is rich in Calcium which is an essential mineral required for bone and teeth development, and also in the regulation of nervous excitability. The oil extracted from garlic bulbs was also characterized. The garlic bulb was discovered to have a high percentage of oil and unsaturated fatty acid (8.40%). The iodine value of the oil was also high (126.9 $\pm$ 0.1), the saponification value was 192 $\pm$ 0.1, which indicate that the oil can be used as food and the acid value was 41.7 $\pm$ 0.1 which shows that the oil is good for human consumption.

Key words: AAS, Garlic Oil, Saponification value, Acid Value, Mineral elements.

INTRODUCTION

Oil is one of the three major classes of food substances; the others are protein and carbohydrates. Garlic oils are naturally occurring esters of glycerol and fatty acids that have commercial uses, some oils are called trimester examples are triglycerides or simple glycerides [1].

Garlic oils are liquid at room temperature; this is because of the type of fatty acids they contain. In general the more saturated fatty acid oils contain, the more solid it will be and the more unsaturated fatty acid the oils contain the more liquid it will be at room temperature [1].

The physical and chemical properties of garlic oils are determined to a large extent by the type of fatty acids in the glycerides. In all commercially important glycerides, the fatty acids are straight chain and nearly all contain even number of carbon atoms.

The majority of oils come from plants sources such as nuts and seeds but garlic oil is extracted from fresh bulb of garlic (Plant) botanically known as *Allium sativum L.*, which is a species in the onion family *Alliaceae*, it's close relatives includes the onions, shallot and the leek [5].

Origin of garlic

Garlic is one of the most commonly used herbs in the world. It is a member of the onion family and has a strong and characteristic odour, which is different in both fresh and fried state. *Alliums longiscuspic* is said to be the wild ancestor of garlic, the name garlic comes from the Anglosaxon 'garleae' in which gar (a spear) refers to the pointed leaves and "leae" is the plant (reference). Garlic was first discovered in Asia and Mediterranean region. Later it was transported to Europe; it was in use in England prior to (1548).

Garlic is said to have been introduced to China in 140 – 86 BC. Garlic was first reported in America in 1806 by Peter Martyr and since then its use spread rapidly to African countries like Egypt, Liberia and Nigeria where it is widely cultivated in the northern Nigeria.

Types of garlic

There are different varieties of garlic due to differences in size, colour, shape, taste and number of cloves per bulb. Garlic is classified into two, the true and the false garlic. The true garlic are the species *Allium Sativum* and there are two sub species of true garlic *Allium sativum* var. *ophioscorodon* (Link) Döll, called Ophioscorodon, or hard necked garlic, includes porcelain garlics, rocambole garlic, and purple stripe garlics. It is sometimes considered to be a separate species, *Allium ophioscorodon* G. Don. *Allium sativum* var. *sativum*, or soft-necked garlic, includes artichoke garlic, silverskin garlic, and creole garlic [7].

Extraction of garlic oil

The extraction of garlic oil is carried out using three extraction techniques namely steam distillation, maceration and modern extraction method.

Steam distillation method

This is used in the extraction of garlic oil, the garlic materials are placed in a still and steam is force over the material. The hot steam helps to release the aromatic molecules from the garlic materials since the steam foces open the pocket in which the oils are kept in the garlic material. The molecules of these volatile oils then escape from the garlic materials and evaporate into steam.

The temperature of the steam need to be carefully controlled just to force the material to let go of the oil yet not too hot to born the garlic material or the garlic oil. The steam, which contains the garlic oil, is passed through a cooling system to condense the steam which form a liquid from which the garlic oil and water is separated.

The steam is produced at a great pressure than the atmospheric pressure and therefore boils at 100^0C which facilitate the removal of the oil from the garlic at a faster rate and in so doing prevents damage to the oil [7].

Steam-distilled garlic oil contain principally allyi sulphide, Allicin is a volatile component of the oil and may be lost or converted to the Allyl sulphide degradation compounds, which usually are diallydisulphide (DADS) or diallytrisulphide (DATS) (Staba, *et al.*, 2001,).

Allicin → DADS or DATS

Maceration

In maceration method, the fresh garlic bulbs are soaked in hot oil to enhance the rupture cell membranes. When the oil absorbs the essence, the oil is then cleared off the garlic material and decanted. Maceration may be hydroalkoholic short or hydroalkoholic long maceration.

Hydroalcoholic short maceration: Here the extraction of fresh or dried garlic with hydroethanoic solution is done for a short maceration time [10].

Hydroalcoholic long maceration: Here sliced garlic is placed in 20% ethanol and maceration for long period of time filtered and concentrated [10] & [12].

Maceration technique is very much the same technique used in solvent extraction, where solvents are used instead of the hot oil as used in maceration. During solvent extraction, non-volatile component of the botanical material such as waxes and pigments are also extracted and in some case, this is then removed during another process. Solvent extraction may also include Effleurage and hypercritical CO_2 (Carbon dioxide). Effleurage could be compared to some certain aspects employed in maceration but it is done in slightly different way while the use of hypercritical carbon dioxide in extraction of essential oil is a fairly new to extract oils although a bit expensive but yield good quality oil.

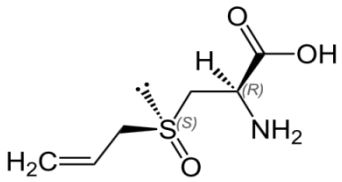
Modern extraction methods

These apply microwave in the extraction of the garlic oil. A comparative study of traditional Simultaneous Distillation Extraction (SDE), Microwave Assisted Hydro – Distillation Extraction (MWHD) carried out by Kumbans, Siatis, Daferera, Taranlilis, Pappas, and Polisson (2005) showed that the highly reactive sulphur molecule of the garlic volatile fraction show variable response to the different methods [4]

Composition of garlic oil

Garlic oil contains the amino acid Alliin ($C_6H_{12}NO_3S$) which is odourless and can be converted to a compound called Allicin. When the garlic is crushed or otherwise damaged the allin react with enzyme Allinase, also found naturally in garlic. Allinase acts as catalyst resulting in the transformation of Alliin to Allicin [8].

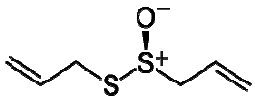
Structure of Alliin



Allicin

Garlic contains allicin ($C_6H_{10}OS_2$) also known as dially thiosulhinate, a powerful antibiotic and antifungal compound, is a product of enzymatic reaction. It does not occur in garlic naturally; instead garlic gloves contain the amino acid allin. Allicin is a sulfinyl compound that gives garlic its strong odor and flavor. The release of allicin occurs after a garlic clove is crushed or finely chopped. Allicin begins to breakdown quickly especially if heated [8].

Structure of Allicin

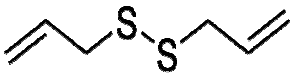


Allicin (2-propene-1-sulphouthioic acid S-2-propen-1ester)

Dially disulphide

Dially disulphides do not have the strong anti-bacterial and antifungal properties of allicin but they are still believed to have medical benefits especially as regards to blood circulation and cholesterol [8].

Structure of Dially disulphide



Other chemical compositions of garlic oil include dially trisulphide, which is about 29.7%. Ajoene which possesses antifungal properties, is an unsaturated disulfide, is formed from a chemical reaction involving two allicin molecules. Subsequent formation of ajoene occurs when allicin is dissolved in various solvents including edible oils. Ajoene is also found in garlic extract. Ajoene is most stable and most abundant in macerate of garlic (chopped garlic in edible oil). Garlic also contain enzymes, vitamin B and minerals [8].

It was discovered in a study on Egyptian garlic, that sulphur-containing main constituents of garlic oils are dially trisulphide (29.7%), dially tetra sulphide (4.4%), dially disulphide (3.7%), dially sulphide (2.5%) methyl allyl trisulphide (2.1%) [9] & [11]

Nutritive value

Garlic oil is a concentrated form of energy substance holding up to 3 cal/g or (10.2 joules/g) as compared to carbohydrate and proteins that holds about 2 cal/g or (4.4 joules/g). Garlic oil makes a meal more satisfying by creating a feeling of fullness [8].

Mineral composition of garlc oil

Minerals are inorganic elements that are found in the body in ionic forms and almost all the metabolic processes are dependent on. The minerals in garlic oil provide the requirements of minerals, by the human body, Garlic in mineral element content of phosphorus was highest, followed by magnesium, calcium, iron, silicon, aluminum and zinc.

MATERIALS AND METHODS

MATERIALS

The Garlic bulbs were obtained from the locally cultivated sourced in Sokoto. The bulbs were dried at room temperature to constant weight. The dried garlic was then ground into powder using motar and pistil. 2.5g of the sample was taken and digested using 25cm3 of concentrated nitric acid and perchloric acid in a beaker. The mixture was heated over heating mantle until all fumes were given off. The mixture was allowed to cool to room temperature and filtered to remove any residue. The filtrate was placed in a 100 cm3 capacity volumetric flask and made up to the mark with distilled water.

METHODS

Atomic Absorption Spectrophotometeric (AAS) method was used to determine the concentration of the minerals. It is an analytical technique which is used to determine the concentrations of elements in gaseous state. The technique makes use of the wavelength of light absorbed by an element which usually corresponds to the energies of excitation needed to promote electrons from ground state to excited state. Samples in aqueous media are aspirated into a high temperature flame. The amount of light absorbed by the element or metal atom is proportional to the concentration of the element, and this relationship is known as Beer-Lambert's Law.

Oil extraction

Crushed fresh garlic is placed in a porous thimble and the thimble is placed in the inner tube of the soxhlet apparatus. The apparatus is fitted with a round bottom flask of appropriate size containing the solvent and then boiled by heating mantle and reflux condenser.

The solvent was then boiled gently and the vapour passes up through the tube and is condensed by the condenser and the condensed solvent fall back into the thimble and slowly fills the body of the soxhlet extractor. The top of the porous thimble should be above the siphon tube otherwise the crushed garlic may tend to float out of the thimble and pass down the siphon tube; also a plug of wool is placed on the mouth of the thimble to prevent the cheff of garlic bulb from falling out. When the solvent reaches the top of the tube it siphons over into the flask and thus remove that portion of the solvent or substance, which it has extracted. Water is connected to the reflux condenser, which helps in condensing the vapour of the solvent thus recycling it. The process is repeated automatically until complete extraction is achieved. The extracted garlic oil is isolated from the solvent which in this case is n-Hexane by evaporation in a boiling water bath.

A) Saponification Value

Is a measure of the mean molecular weight of the fatty acids present in the garlic oil, the process of saponification is the hydrolysis of triglycerides into glycerol and the potassium salt of the acids using a solution of potassium hydroxide in ethanol. The saponification value thus is being expressed as the number of milligrams of potassium hydroxide required to saponify one gram (1g) of the garlic oil. The details of individual standard method vary but the general technique is similar to B.S.I method. It is necessary to carry out a blank test simultaneously with the samples. About 7g of the garlic oil are accurately weighed into a flask. To this 25cm^3 of ethanolic potassium hydroxide are added, a "blank" prepared by putting 25cm^3 of the ethanolic potassium hydroxide in a similar flask. Air condenser is fitted to both flask and the contents were boiled for one hour, swirling the flask from time to time. The flask is then allowed to cool a little and the condenser is washed down with a little distilled water the excess potassium hydroxide is titrated with 0.5M hydrochloric acid using phenolphthalein indicator, the saponification valve is calculated from difference between the blank and the same titration.

$$\text{Saponification value} = \frac{28.05\text{x}(\text{blank titration} - \text{samples titration})}{\text{Weight of sample}}$$

Where 28.05 is the number of milligrams of KOH in 1cm^3 of 0.5M potassium hydroxide

B) Iodine Value

Is a measure of the proportion of unsaturated acid present; from the test carried out was no presence of unsaturated acid in garlic oil, but the test measure the amount of iodine which can be absorbed by the unsaturated acids. The determination of iodine value is based on the absorption of the halogen by the unsaturated fatty acids the variation in the method has arisen because no one method is fully satisfactory under all condition probably the most widely used is that devised by Wij's and described here. The garlic oil is dissolved in 20cm^3 of carbon tetrachloride and 75cm^3 of Wij's solution is added from a pipette. A blank titration is done alongside the same flask using the same pipette. The stoppered flasks were swirled to mix the content and placed in a dark cupboard for 30 minutes at room temperature. They were then removed and to each 20cm^3 of potassium iodide solution was added, followed by 100cm^3 of distilled

water. The liberated iodine is slowly titrated with 0.1M $Na_2S_2O_3$, until the yellow colour just disappeared. At this stage 2cm^3 of starch solution are added and blue colour appears which is discharged by further slow addition of thiosulphate.

$$\text{Iodine value} = \frac{(\text{blank titration} - \text{sample titr.}) \times \text{molarity of } Na_2S_2O_3 \times 126.9}{\text{Weight of sample}}$$

C) Acid Value and Free Fatty Acids

This is a measure of the amount of free fatty acids present in garlic oil which is given percentage. The acid value is the number of milligram of potassium hydroxide required to neutralized 1g of garlic oils. The degree of acidity is a number of milligrams of sodium hydroxide required to neutralize 100g of the garlic oil. Ethanol is boiled on water bath for few minutes to remove dissolved gasses and neutralized by adding a few drops of phenolphthalein and dilute NaOH, until a pink colour is obtained. 7g of the garlic oil was weighed into the flask and about 25cm^3 of the hot neutralize ethanol is added and the mixture boiled on a water bath, while still hot, the solution is titrated with 0.1M NaOH solution until the pink colour returns. The amount of NaOH used is recorded to be 20cm^3..

$$\text{Free fatty acids} = \frac{\text{Titration} \times 282 \times 100}{1000 \times 10 \times \text{wt of sample}}$$

The acid value is a simpler expression, as the calculation is independent of the molecular weight of the fatty acids. The acid value is calculated by

$$\text{Acid value} = \frac{5.61 \times \text{titration}}{\text{Weight of sample}}$$

D) Oil Yield Determination

Garlic oil is all the substance that was extracted under the operating condition specified in the test method. The oil content is expressed as a percentage by mass of the garlic bulb as used for the extraction. The grounded sample was transferred into extraction thimble, which is placed in the soxhlet extractor provided with 250cm^3 flasks and an electric heating bath. The garlic oil is extracted by gentle boiling hexane (150cm^3) in a weighed flask A. after the extraction for four hours the thimble is removed and the greater part of the solvent evaporated in a current of air. Another extraction with 150cm^3 hexane in flask B is carried out for another four hours. The greater part of the solvent from flask A and flask B is removed by heating the oil on heating plate which enable the solvent (n-hexane) vaporize. At this stage the last traces of hexane is removed, after cooling the flask and oil the flask are weighed and heating is repeated under the same condition for 10 minutes to enable constant weight. Hence, the oil determination by direct extraction is calculated as thus:

The sum of the mass of the oil from flask A and B = W and the mass of the test portion = W_o

$$\text{Oil content (\%) of the material as received} = \frac{100 \times W}{W_o}$$

RESULTS AND DISCUSSION

The results of the chemical analysis carried out on the garlic bulb oil are represented in table 3.1 and 3.2 respectively.

TABLE 1 Physical properties of garlic oil.

Parameters	Results
Colour of oil extracted	Light yellow
Specific gravity	0.90g $\pm$ 0.01
Odour	Pronounced odour
Oil yield	21.6%
Boiling point	115^{0}C

TABLE .2: Chemical properties of garlic oil

Parameters	Results
Free fatty acid (%oleic acid)	8.40%
Iodine value (g/100g)	126.9 ± 0.1
Saponification value (mg/KOH/g)	192 ± 0.1
Acid value (mg/KOH/g)	41.7 ± 0.1

TABLE 3: Mineral elements concentrations in Garlic

Mineral Elements	Concentration(mg/L)	% composition
Ca	6.770	0.277
P	0.32	0.013
K	62.22	2.489
Mg	27.60	1.104
Mn	0.060	0.0024
Cu	0.030	0.0012

DISCUSSION

The oil contains a high proportion of unsaturated fatty acids like oleic acid and linoleic acid, oil which contain more than 7%. Linoleic acid cannot be use for frying, because they oxidize readily, yielding suspect products (e.g irritant) they can only be used for light cooking less than 15^0C [7].

The percentage yield was 21.6% indicating that the garlic bulb can be used as a source of oil on commercial scale. The colour observed from the crude garlic oil was light yellow and has a pronounced odour. However the oil is liquid at room temperature indicating the presence of oleic acid and linonleic acid and other unsaturated fatty acids [8]. Thus the garlic bulb is an oil source just like cotton seeds.

Saponification value

It is a measure of the average molecular weight (or chain length) of all the fatty acids present. As most of the mass of a fat/triester is in the 3 fatty acids, it allows for comparison of the average fatty acid chain length. The long chain fatty acids found in fats have a low saponification value because they have a relatively fewer number of carboxylic functional groups per unit mass of the fat as compared to short chain fatty acids. If more moles of base are required to saponify N grams of fat then there are more moles of the fat and the chain lengths are relatively small [2]. The saponification value of the garlic was found to be 192mg/KOH/g the saponification value obtained in the oil under the study suggests that it contains short chain fatty acids.

The acid value, which is an index of free fatty acid content due to enzymatic activities in the garlic bulb was found to be 8.40 mg/NaOH/g. the acceptable value of 6 mg/ NaOH /g recommended by the codex alimenterios commission for sun flower oil [2]. This value shows that the oil does not have long shelve life as it can rapidly go rancid.

Specific gravity, this is defined as the ratio of the density of a material to the density of some standard material usually water at 4^0C. However, the density obtained was 0.90g/cm^3, which is comparable to those of *Albizia lebbeck* seed oil (0.70m/cm^3) but less dense than those of *Acacia nilotica* seed oil (0.9g/cm^3) [4]. Iodine value is the measure of the proportion of unsaturated acids present in oil. The iodine value of the garlic oil 126.9g/100g, which is high indication that it is drying oil. The value is higher than the iodine value of African pear (121.03) [5].

Boiling point of the oil is the temperature at which the saturated vapour pressure of the oil becomes equal to the atmospheric pressure[4]. The boiling point of 155^0C for the oil indicates that it has molecular weight than water which boils at 100^0C.

The result of AAS analysis revealed that garlic is rich in minerals such as Ca, P, K, Mn and Cu. Garlic contain a high proportion of K (2.485%) followed by Mg (1.104%) and these was followed by Ca (0.277%) . It also contain P, Mn and Cu (0.013) (0.0024) and (0.0012) respectively. This made Garlic a very valuable source of minerals. The results obtained indicates that garlic is rich in Calcium which is an essential mineral required for bone and teeth development, and also in the regulation of nervous excitability. Sokoto garlic is rich in Phosphorus which is a key component of the nucleic acids and also takes part in bone and teeth development; and Copper which plays an important part in blood clotting. Manganese is used in proper bone formation.

CONCLUSION

From the results, it can be concluded that Garlic is a good source of minerals and oil. It a major food additive in and around northern Nigeria. The oil content is also high which makes it's extraction in commercial quantity profitable. The oil also is a very high quality for human use since it has a high proportion of unsaturated fatty acids.

Recommendation
Garlic oil has high linolic acid content and is therefore advice as suitable dietary oil in condition of heart disease and high blood pressure.

As regards nutritional aspect, we are all aware of the encouragement given by various authoritative bodies throughout the world to decreasing total fat intake and increasing the proportion of unsaturated fat of which garlic oil is a very good example. It is also recommended based on its minerals content.

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