COMPARATIVE ANALYSIS OF THE MINERAL COMPOSITIONS OF HONEY SAMPLES COLLECTED FROM THE THREE SENATORIAL DISTRICTS OF KANO STATE, NIGERIA

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ABSTRACT

Honey is widely used as food and as sweetening agent. Honey is also known to have many medicinal applications including antimicrobial, antibacterial, antifungal, anti-inflammatory and antioxidant activities. The composition of honey may vary due to geographical location, environmental and climatic conditions, plant species, as well as the methods employed during collection and storage of the honey. Honey contains different types of proteins, hormones, enzymes, vitamins, minerals, yeast, as well as organic acids, and principally sugars. This study was conducted in order to analyze and compare the mineral contents of the honey samples collected at the three senatorial districts of Kano state, with three honey samples collected from two local governments each from the three Senatorial Districts of Kano State, Nigeria. The mineral compositions of all the honey samples were determined using flame photometer and atomic absorption spectrophotometer. All the honey samples analyzed were found to be rich in K (247.49 to 251.73 µg/g); Na (137.16 to 147.53 µg/g); Ca (188.57 to 221.32 µg/g); Mg (76.49 to 78.83 µg/g) and Zn (31.15 to 48.92 µg/g), while Fe (6.84 to 14.27 µg/g); Mn (0.08 to 0.13 µg/g); Cu (0.12 to 0.25 µg/g); Ni (0.98 to 1.27 µg/g) and Pb (not detectable to 0.0002 µg/g) were found in smaller concentrations. The mineral compositions of all the honey samples were found to meet the international honey standards, and are therefore suitable for human consumption.

Keywords: Honey, mineral composition, medicinal application, senatorial districts.

INTRODUCTION

Honey is a unique, natural, liquid sweetening agent produced by honey bees (Apis mellifera) from the nectar of plants or from honeydew (Codex Alimentarius 2002; El-Bialee and Sorour 2011; Adunaga et al., 2020). The composition of honey may vary due to geographical location, environmental and climatic conditions, plant species, as well as the methods employed during collection and storage of the honey (De Rodriguez et al., 2004; Kucuk et al., 2007; Lalae et al., 2013). However, generally honey contains different types of proteins, hormones, enzymes, vitamins, minerals, yeast, some heavy metals, as well as organic acids, and principally sugars (Hernandez et al., 2005; Kujawski and Namiesnik 2008; Pohl 2009; Wang and Li 2011; Adunaga et al., 2020). The organic acids are mainly pyruvic, lactic and formic (Bogdanov 2009). The physicochemical parameters of honeys have been strictly defined and serve as quality indicators of individual honeys, with honeys of same variety having similar physicochemical parameters (Juszczak et al., 2009; Lalae 2013). Numerous researches have been conducted (Adebiyi et al., 2004; Rodriguez et al., 2004; Downey et al., 2005; Finola et al., 2007; Al et al., 2009; Juszczak et al., 2009; Ajlouni and Sujirapinyokul 2010; Abel and Adedoyin 2011; Laleh et al., 2013; Adeniyi et al., 2014; Boussaid et al., 2018; Adunaga 2020) and many are still on-going, to determine the physicochemical properties of honeys.

Even though honey is widely used as food and as sweetening agent, it is also known to have many medicinal applications (Farida et al., 2014). Honey was reported to exhibit healing powers in the treatments of many disorders (Gulfraz et al., 2010), with its antimicrobial, antibacterial, antifungal, anti-inflammatory and antioxidant activities also reported (Omafuvbe and Akanbi 2009; Gomes et al., 2010; Gulfrast et al., 2010; Kumar et al., 2013).

Knowledge of the nutritional value and the possible toxicological constituents of all local food substances is of utmost importance (Nnam 2003), as this will help eliminate all dietary problems associate with the deficiencies of such food substances (SCN 2006). Thus, the present study was conducted to analyze and compare the mineral contents of the honey samples collected the three senatorial districts of Kano state.

MATERIALS AND METHODS

Samples Collection

Three honey samples were collected from two local governments each from the three Senatorial Districts of Kano state, Nigeria. The samples were stored in clean airtight bottles at an ambient temperature to avoid growth of microorganisms as well as absorption of moisture (Gulfraz et al., 2010; Laleh et al., 2013). The samples were collected from the following areas: Kano Central (Dawakin Kudu and Ungogo); Kano South (Bebeji and Ajingi); Kano North (Gwarzo and Makoda), and all the honey samples were collected directly from the honey bee farmers.

Determination of Mineral Composition

To carry out the digestion of the honey samples, 1 g of each of the honey samples was weighed, homogenized, and placed in a conical flask. Concentrated nitric acid (8 mls) and hydrogen peroxide (4 mls) were added on to the sample in the conical

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The mixture was then placed on a water-bath and heated for 4 hr to dryness, and then the flask was removed and cooled to room temperature. De-ionized water was then added to the sample in order to dissolve the dried substance (Tuzen et al., 2007; Adugna et al., 2020). The content was then filtered using Whatman no. 42 filter paper into a clean volumetric flask (10 ml), and subsequently the solution was made up to the volume with de-ionized water. Using the same procedure, the reagent blank was prepared using the reagents, concentrated nitric acid and hydrogen peroxide, and then treating them in similar way as the samples (Tuzen et al., 2007; Adugna et al., 2020).

The mineral compositions of all the honey samples were determined using flame photometer (Model: Buck VGP 410) and atomic absorption spectrophotometer (Model: Bulk VGP 210). Potassium (K) and sodium (Na), calcium (Ca), magnesium (Mg), zinc (Zn) and iron (Fe) were analyzed by flame atomic absorption spectrometry (FAAS), while manganese (Mn), copper (Cu), nickel (Ni) and lead (Pb) were analyzed by atomic absorption spectrometry (AAS) as reported by Mohammed et al., (2014) and Oyeyemi et al., (2015).

### RESULTS AND DISCUSSION

**Results**

The mineral compositions of all the honey samples analyzed are presented in Table 1 below.

**Table 1: Mineral Compositions of the Honey Samples**

| Sample   | K (µg/g) | Na (µg/g) | Ca (µg/g) | Mg (µg/g) | Zn (µg/g) | Fe (µg/g) | Mn (µg/g) | Cu (µg/g) | Ni (µg/g) | Pb (µg/g) |
|----------|----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|-----------|
| KC A     | 251.73   | 146.94    | 188.57    | 76.49     | 33.37     | 6.84      | 0.08      | 0.13      | 0.98      | 0.0002    |
| KC B     | 249.91   | 147.53    | 193.68    | 78.21     | 31.15     | 8.11      | 0.11      | 0.16      | 1.27      | 0.0001    |
| KS A     | 247.49   | 139.51    | 217.09    | 77.63     | 41.07     | 12.36     | 0.09      | 0.21      | 1.09      | 0.0001    |
| KS B     | 248.12   | 140.29    | 221.32    | 76.59     | 39.79     | 14.27     | 0.12      | 0.25      | 1.06      | ND        |
| KN A     | 249.37   | 137.16    | 197.95    | 77.18     | 37.34     | 11.79     | 0.12      | 0.12      | 1.21      | ND        |
| KN B     | 248.76   | 138.93    | 199.87    | 78.83     | 48.92     | 9.85      | 0.13      | 0.13      | 1.25      | ND        |
| WHO/     | 3500 to 1500 to 300 to 26 to 260 | 350 to 13.7 to 5.0 to 0.0 to 0.0 | 0.0 to 0.0 to 0.0 to 0.0 to 0.0 | 0.0 to 0.0 to 0.0 to 0.0 to 0.0 | 0.0 to 0.0 to 0.0 to 0.0 to 0.0 | 0.0 to 0.0 to 0.0 to 0.0 to 0.0 | 0.0 to 0.0 to 0.0 to 0.0 to 0.0 | 0.0 to 0.0 to 0.0 to 0.0 to 0.0 | 0.0 to 0.0 to 0.0 to 0.0 to 0.0 | 0.0 to 0.0 to 0.0 to 0.0 to 0.0 |
| FAO      | 4700     | 2300      | 1300      | 1000      | 0.5 µg/g  | 20.5 µg/g | 0.0002    | 0.0002    | 0.0002    | 0.0002    |

Key: KC A = Dawakin Kudu; KC B = Ungogo; KS A = Bebeji; KS B = Ajingi; KN A = Gwarzo; KN B = Makoda; ND = Not Detected

**DISCUSSION**

The differences in the minerals concentrations in the honey samples can be attributed to variations in the botanical and geographical origins of the honeys, (Rasheed and Soltan 2004), as well as environmental pollution, and the differences in beekeeping practices and processing (Pohl 2009).

Potassium is the third most abundant mineral in the body and helps the body regulate fluid, send nerve signals, regulate muscle contractions, maintain a regular heartbeat (Aburto et al., 2013) and also helps in preventing kidney stones (Kama et al., 2013). Potassium is also known to help in reducing blood pressure, protects against stroke and prevents osteoporosis (Raman 2017). The concentrations of potassium in all the honey samples analyzed in this study fall between 247.49 µg/g (Bebeji honey) to 251.73 µg/g (Dawakin Kudu honey), and these results are in agreement with similar results reported by Pisani et al., (2008); Adeniyi et al., (2014); Mohammad et al., (2014) and Nwoko et al., (2017). However, the results are higher than those reported by Kumar et al., (2013); Oyeyemi et al., (2013); Ndife et al., (2014); Saeed et al., (2014); Ahmed and Khalid (2017) and Nwoko et al., (2017), with the discrepancy possibly attributed to the geographical variation in the location of the honey sources (Conti 2000). However, the results compare with similar reports by Adebiyi et al., (2004); Saxena et al., (2010); Vanhanen et al., (2011); Oyeyemi et al., (2013); Boussaid et al., (2018); Ezeh et al., (2018).

Calcium is the most important and most plentiful mineral found in the human body that forms and maintains healthy teeth and bones, as well as prevents osteoporosis (Turan et al., 2003; Piste et al., 2013). Calcium also helps in clotting of blood, sending and receiving nerve signals, squeezing and relaxing muscles, and helps in keeping a normal heartbeat (Piste et al., 2013). Calcium is the second most abundant mineral in honey (Adebiyi et al., 2004; Boussaid et al., 2014; Ahmed and Khalid (2017), and this supports the present study that recorded the concentration of calcium second to that of potassium. All the samples analyzed in this study recorded a high calcium content ranging from 188.57 µg/g (Dawakin Kudu honey) to 221.32 µg/g (Ajingi honey), with these results similar to that reported by Adebiyi et al., (2004); Agbagwa et al. (2011); Kumar et al., (2013); Oyeyemi et al., (2015). However, the results are much higher than that reported by Conti (2000); Adeniyi et al., (2014); Ndife et al., (2014); Ahmed and Khalid (2017); Nwoko et al., (2017), but lower than that reported by Gulfaraz et al., (2010).

Magnesium is another abundant mineral in the body that is naturally present in many foods, and is a cofactor in more than 300 enzyme systems that regulate many biochemical reactions in the body (Rude 2012; Volpe 2012), as well as energy production, oxidative phosphorylation and glycolysis, as well as transportation of calcium and potassium ions across cell membranes. However, the results are higher than that reported by Kumar et al., (2013); Adeniyi et al., (2014); Mohammad et al., (2014); Ndife et al., (2014); Saeed et al., (2014); Ahmed and Khalid (2017) and Nwoko et al., (2017), with the discrepancy possibly attributed to the geographical variation in the location of the honey sources (Conti 2000). However, the results compare with similar reports by Adebiyi et al., (2004); Saxena et al., (2010); Vanhanen et al., (2011); Oyeyemi et al., (2013); Boussaid et al., (2018); Ezeh et al., (2018).
membranes (Volpe 2012). Mild deficiency of magnesium may lead to loss of appetite, nausea, vomiting, fatigue, and weakness, while severe deficiency leads to tingling, numbness, muscle contractions and cramps, seizures, poor bone growth, joint pains, fertility problems, abnormal heart rhythms and coronary spasms can occur (Rude 2012; Emmanuel et al., 2018). The results from the present study show a range between 76.49 µg/g (Dawakin Kudu honey) to 78.83 µg/g (Makoda honey) for the pure honey samples analyzed, and this agrees with similar result by Boussaid et al. (2018) who reported a range of 74.90 to 78.12 µg/g for six honey samples from Tunisia. Other results similar to this study were reported by Fernandez-Torres et al., (2005); Pisani et al., (2008); Chua et al., (2012); Mohammed et al., (2014); Vanhanen et al., (2011); Bontempo et al., (2017); Altunmataz et al., (2018). Lower magnesium concentrations in honey samples were however reported by Liberato et al., (2012); Adeniyi et al., (2014); Ndife et al., (2014); Ahed and Khalid (2017); Nwoko et al., (2017).

Zinc is a trace element that is necessary for a healthy immune system, with its deficiency making a person more susceptible to disease and illness (Haase and Schomburg 2019). Zinc has many functions in the human body. It helps in stimulating the activities of many different enzymes in the body, plays a role in wound healing, and in the treatment to diarrhea (Mason 2016; Salwen 2017). In this study, a range of 31.15 µg/g (Ungogo honey) to 48.92 µg/g (Makoda honey) was reported for zinc in the six pure honey samples analyzes, and these results are within the 1.734 to 245.205 µg/g range reported by Altunmataz et al., (2018) for 65 honey varieties produced in Turkey. The results of this study also agree with that reported by Bartha et al., (2020) who reported a range of 15.00 to 36.40 µg/g for some honey samples from Romania. The results from this study are also close to that reported by Celechovska and Vorlova (2001); Tuzen and Soylak (2005); Gulfraz et al., (2010); Mohammed et al., (2014); Ezeh et al., (2018); Adugna et al., (2020). However, the results from this study are found to be much higher than that reported by other researchers (Turhan, 2007; Tuzen et al., 2007; Kolayli et al., 2008; Kumar et al., 2013; Mohammed et al., 2014; Aghamirlo et al., 2015; Sireli et al., 2015; Nwoko et al., 2017).

While Oyeyemi et al., (2015) reported a value of 124.24 µg/g, which is much higher than that of this study. The 33.37 to 48.92 µg/g range reported in this study is below the maximum permissible limit (350 µg/g) recommended by Codex Alimentarius Commission (2002).

Iron is an essential nutrient mineral that serves several important functions, but its main function is to carry oxygen throughout our bodies and making red blood cells (Beard and Dawson 1997). Iron is an essential element for almost all living organisms as it participates in a wide variety of metabolic functions, but its main function is to carry oxygen throughout our bodies and making red blood cells (Beard and Dawson 1997). The concentration of iron in the six honey samples analyzed in this study was found to be between 6.84 µg/g (Dawakin Kudu honey) to 14.27 µg/g (Ajingi honey) range, and this result compares with similar results reported by Nanda et al., (2003); Adebisi et al., (2004); Atrouse et al., (2004); Terrah et al., (2005); Yarsan et al., (2007); Pisani et al., (2008); Ahed and Khalid (2012); Liberato et al., (2012); Kumar et al., (2013) and Altunmataz et al., (2018). However, the results from study was found to be much lower than that reported by Mohammed et al., (2014) who reported a very high iron content of 162.31 µg/g; and that reported by Oyeyemi et al., (2015) who reported a value of 171.52 µg/g for honey samples collected from Ekiti State, Nigeria. While on another hand, the results of this are much higher than that reported by Adeniyi et al., (2014); Maiyo et al., (2014); Ndife et al., (2014) and Boussaid et al., (2018).

Manganese is required for enzyme functioning in the body, wound healing, prevention of anemia, nutrient absorption, alleviating premenstrual syndrome, bone development and antioxidiant protection, with its deficiency resulting in poor bone growth, joints pains and fertility problems (Emmanuel et al., 2018). However, when exposed for a very long time, manganese causes impotency in men and also Parkinson disease (Emmanuel et al., 2018), as such honey should not contain high concentration on manganese. The concentrations of manganese in the six pure honey samples were found to be between 0.08 µg/g (Dawakin Kudu honey) to 0.13 µg/g (Makoda honey) range, and these results are far below the FAO/WHO maximum permissible limit of 5.50 µg/g. The findings in this study compare with similar results from other researchers (Fernandez-Torres et al., 2005; Fredes and Montenegro 2006; Belouali et al., 2008; Liberato et al., 2013; Doker et al., 2014; Czipa et al., 2015; Oroian et al., 2016; Ahed and Khalid 2017; Bilandzic et al., 2017; Khilc et al., 2017; Altunmataz et al., 2018. The results from the present study are however much lower than those reported by Rasheed and Soltan (2004); Golob et al., (2005); Turhan (2007); Tuzen et al. (2007); Kolayli et al., (2008); Chua et al., (2012); Bontempo et al., (2017). High levels of manganese in some honey samples may be attributed to its presence in the dust through the air, surface waters, burning of fossil fuels and industrial activities (Emmanuel et al., 2018).

Copper is one of the essential trace minerals necessary for survival, and is found in almost all the body tissues, playing a role in maintaining nerve cells and the immune system, as well as in making red blood cells and (Megan 2017). It is also believed to play a major role in the formation collagen, helps in iron absorption and in the production of body energy, with too much and too little copper reported to affect how the brain works (Megan 2017). The concentration of copper in the present study was found to be between the range of 0.12 µg/g (Gwarzo honey) to 0.25 µg/g (Ajingi honey), and this compares with similar results reported by Celechovska and Vorlova (2001); Devillers et al., (2002); Tuzen and Soylak (2005); Akbari et al., (2012); Derebas et al., (2014), while some researchers (Roman et al., 2011; Dzugan et al., 2017) have reported much higher concentrations. The concentrations of copper in the six pure honey samples analysed in this study were found to be far below the FAO/WHO maximum permissible limit of 300 µg/g.

Nickel is an essential trace element for both human and animal health (Zaigham et al., 2012) that is required in small doses, but can be hazardous at very high doses (Sreekanth et al., 2013). The carcinogenic effect of nickel at higher doses has been reported to cause cancer of the larynx, nose, lungs and prostate, as well as birth defect, lung embolism, respiratory failure, asthma and bronchitis (Zaigham et al., 2012; Guodong et al., 2017). The concentrations of nickel analyzed in this study were...
found to be between the range of 0.98 µg/g (Dawakin Kudu honey) to 1.27 µg/g (Ungogo honey), and all these results are far below the WHO/FAO maximum permissible limit for nickel (5.0 µg/g). The results of this study also fall within the range of 0.39–8.60 µg/g reported by Ahed and Khalid (2017), with Aghamirloiu et al., (2015) also reporting the mean concentration of nickel for honey samples from Iran as 0.91 µg/g. The results from the present study are a little higher than 0.480 µg/g reported by Sobhanardakani and Kiampour (2016) for honey samples collected in Turkey. However, the results are lower than that reported by Emmanuel et al., (2018) who reported the mean concentration of nickel in some honey samples to be between the range of 1.200 to 44.100 µg/g. Presence of nickel in honey might not be as significant as other metals because some honey samples have been reported to contain non-detectable amount of nickel (Adugna et al., 2020).

Lead is a non-essential metal with no physiological role in both plants and animals (Bartha et al., 2020), with its exposure occurring through contacts with water, air, soil and contaminated food (Kabata-Pendias 2010; Bartha et al., 2020). Exposure to lead causes neurological effects, renal tubular dysfunction, anemia, nephropathy, as well as impairment of reproductive functions (HPA 2016; Bartha et al., 2020). Accumulation of lead in the environment mainly occurs as a result of melting and production of metals, mining, as well as its release from some industries like the battery industry (Bartha et al., 2020). In this study, three of the six honey samples analyzed (Ajingi, Gwarzo and Makoda honeys) recorded a non-detectable concentration of lead, while the other three recorded a range of 0.0001 µg/g (Ungogo and Bebeji honeys) to 0.0002 µg/g (Dawakin Kudu honey). The results from this study partially agree with similar results by Okeola et al., (2020) who reported a non-detectable concentration of lead in all the analyzed honey samples collected from Ilorin Kwara state, Nigeria, with Nascimento et al., (2015) also reporting similar results. However, the results from this study are found to be much lower than that reported by other researchers (Mayo et al., 2014; Aghamirloiu et al., 2015; Altunatmaz et al., 2018). The concentrations of lead in the six pure honey samples analysed in this study were found to be far below the FAO/WHO maximum permissible limit of 0.50 µg/g.

CONCLUSION
The six honey samples were collected from the three Senatorial Districts of Kano state, Nigeria, and were subjected to mineral contents analysis. Metals (K, Na, Ca, Mg, Zn, Fe, Mn, Cu, Ni and Pb) concentrations were determined, and the values were found to be below the WHO/FAO recommendations. However, there are some little variations between the results of the three Senatorial Districts, with such variations attributed to plant source of the nectar, geographical factors, and nearness of the honey bee source, as well as soil composition and collection techniques.

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