FUDMA Journal of Sciences (FJS)
ISSN online: 2616-1370
ISSN print: 2645 - 2944
Vol. 4 No. 3, September, 2020, pp 170 – 177
DOI: https://doi.org/10.33003/fjs-2020-0403-267

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, the unique, natural, liquid sweetening agent is produced by honey bees from the nectar of plants or from honeydew. 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.

NTRODUCTION

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; Adugna *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; Laleh *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; Adugna *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; Laleh 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; Adugna 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; Gulfraz *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

flask. 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 mls), and subsequently the solution was made up to the volume with the 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/ FAO	3500 to 4700 mg/day	1500 to 2300 mg/day	300 to 1300 mg/day	26 to 260 mg/day	350 µg/g	13.7 to 20.5 mg/day	5.50 µg/g	300 µg/g	5.00 µg/g	0.50 µg/g

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 (Kanu *et al.,* 2013). Potassium is also known to help in reducing reduces 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); Ahed and Khalid (2017), while on the other hand, Conti (2000); Downey *et al.,* (2005) and Terrab *et al.,* (2005) have reported much higher results than that of the present study. Sodium is an essential electrolyte that helps maintain the balance of water in and around our cells. It is important for proper muscle and nerve function, and also helps maintain stable blood pressure levels, with its deficiency or low levels in our bodies requiring medical emergency, as it can cause irritability, weakness, fatigue, loss of consciousness, seizures, coma, etc. (Kim 2019). The concentrations of sodium in the honey samples analyzed in the present study were found to range from 137.16 µg/g (Gwarzo honey) to 147.53 µg/g (Ungogo honey), and these 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); Ahed 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; Ahed 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); Ahed 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 (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, joints 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 Tunusia. 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); Altunatmaz *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 Altunatmaz *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; Aghamirlou *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 processes, including deoxyribonucleic acid (DNA) synthesis and electron transport (Abbaspour *et al.,* 2014). Iron deficiency occurs when the body does not have enough of the mineral iron, and this leads to abnormally low levels of red blood cells (Haas and Brownlie, 2001). 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); Adebiyi *et al.,* (2004); Atrouse *et al.,* (2004); Terrab *et al.,* (2005); Yarsan *et al.,* (2007); Pisani *et al.,* (2008); Ahed and Khalil (2012); Liberato *et al.,* (2012); Kumar *et al.,* (2013) and Altunatmaz *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 antioxidant 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; Kılıc *et al.,* 2017; Altunatmaz *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); Derebasi *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 harzardous 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 Aghamirlou *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 Kianpour (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 (Maiyo *et al.,* 2014; Aghamirlou *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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