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Study and Estimation of Some Elements Content in Libyan Honey

Abd-Alslam H. Azzouz[1] , *Azzelden Elgool*[2] , *Anwar Abd Alraheem*[3]

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[1]*Department of Chemistry , Faculty of Science , Benghazi University-Libya*
[2] *Department of Chemistry, Faculty of Education,Tobruk University-Libya.*
[3]*Environmental Sciences Department, Faculty of Natural Resources and Environmental Sciences, Tobruk University- Libya.*

anwar74@tu.edu.ly

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ABSTRACT

The chemical composition of bee honey varies with the surrounding environment (botanical source and geographical origin), which reflects the nutritional value of honey. Accordingly, twenty Libyan honey samples were collected through the period 2016–2017 from different areas in Libya as the honey samples under study. Eight elements, including K, Na, Ca, Mg, Fe, Zn, Cu, and Mn, have been analyzed using electrothermal atomic absorption spectrometry. Also, statistical analysis of these elements has been performed to determine the present correlation between geographical origin and variation in locations of these elements from one sample to another. In addition, pollen grain analysis was performed for all honey samples to evaluate the botanical source of each sample and interpret the variations in elemental content (nutrition value) from one sample to another. These elements were returned in the ranges (mg/kg) as follows: K: 253.6–4675.5; Na: 41.0–588.0; Ca: 41.0–801.0; Mg: 7.2–44.05; Fe: 4.45–7.9; Zn: 1.05–7.75; Cu: 0.505–1.48; and Mn: 0.95–1.65 mg/kg. With regard to these elements, concentrations were compatible with several international honeys, with some discrimination in some samples.

دراسة وتقدير بعض العناصر الموجودة في العسل الليبي

عبدالسلام حسن عزوز[1]، عزالدين خيرالله عبدالعالي الغول[2]، أنور عبدالرحيم صالح عبدالرحيم[3]

يختلف التركيب الكيميائي لعسل النحل باختلاف البيئة المحيطة (المصدر النباتي والأصل الجغرافي) مما يعكس القيمة الغذائية للعسل. وعليه، تم جمع عشرين عينة عسل ليبي خلال الفترة 2016-2017 من مناطق مختلفة في ليبيا كعينة عسل تحت الدراسة. تم تحليل ثمانية عناصر وهي K، Na، Ca، Mg، Fe، Zn، Cu، Mn. باستخدام مطياف الامتصاص الذري الكهرو حراري . كما تم إجراء تحليل إحصائي لهذه العناصر لتحديد العلاقة الحالية بين الأصل الجغرافي والتباين في مواقع هذه العناصر من عينة إلى أخرى. بالإضافة إلى ذلك، تم إجراء تحليل حبوب اللقاح لجميع عينات العسل لتقييم المصدر النباتي لكل عينة وتفسير الاختلافات في المحتوى الأولي (القيمة الغذائية) من عينة إلى أخرى. تراوحت قيم هذه العناصر في المدى (ملغم / كغم) على النحو التالي: K: 253.6-4675.5، Na: 41.0-588.0، Ca: 41.0-801.0، Mg: 7.2-44.05، Fe: 4.45-7.9، Zn: 1.05-7.75، Cu: 0.505-1.48، Mn: 0.95-65.1 ملغم/كغم.

INTRODUCTION

Honey bees are economically most crucial eusocial insects to our ecosystem and food supply due to their pollination activities (Lawal and Banjo, 2010). They produce honey, royal jelly, bee wax, beebread, propolis, and bee venom. Adult bees and larvae depend on minerals and nutrients for development and reproduction (Ahmad et al., 2020). Is the primary source of carbohydrates, and bee bread (a mixture of pollen and honey) is the primary source of protein, fats, vitamins and minerals (Wright et al., 2018). Pollen has a more diverse (K, P, S, Ca, Mg, Na, Cu, Fe, Mn, Zn) and a more concentrated mineral profile (2.5–6.5% total ash) than nectar or honey [Graham, 2010]. The mineral contents of pollen depend on soil and botanical origin, season and geographical location (Filipiak *et at.,* 2017).

Honey, the popular sweetener throughout the world, is made by bees from nectar extracted from the nectarines of flowers. From ancient times, honey was used both as a natural sweetener and, as a healing agent (Bobis *et al.,* 2020). The composition and flavor of honey varies, depending mainly on the source of the nectar (s) from which it originates and to a lesser extent on certain external factors – climate conditions and beekeeping practices in removing and extracting honey (White, 1975). There are large volumes of data on the characterization of honeys from North America, Europe, Australia, India and South Africa, while there is a paucity of data on Libyan honeys.

In our present work, the results of our preliminary studies have been obtained during the investigation of Libyan honey samples taken from sixteen locations in the east, two locations in the west and two locations in the southwest regions of Libya.

EXPERIMENTAL

Sampling:

The samples were collected through 2017, except two samples through 2016 from different areas in Libya : East regions (Elqwarsha, Ras Elhelal, Sousa, Wadi Alkoof, Jurds, Elhemida, Taknis,Deryana, Elabiar, Benqerdan, Elmari, Ejdabia) samples 2–16 ; west regions (Qasr Elshrief, Masallata, Mesrata) samples 1,17 and 18 ; southeast region (Tazerbo) samples 19 and 20 ; southwest region (Aobari).

Analysis:

About 1 gm a representative sample was measured using an analytical sensitive balance and transferred to 25 ml volumetric flask, heated in a water bath to decrease the viscosity, 0.25 ml of nitric acid and 2.5 ml of concentrated hydrogen peroxide were added, followed by 0.1 ml of ammonium dihydrogen phosphate to those samples being analyzed eight elements (K, Na, Ca, Mg, Fe, Zn, Cu and Mn). Then the samples were diluted with 25 ml of de-ionized water and were solicited for 5 minutes with continuous stirring. Finally the samples were analyzed using the graphite furnace micro atomic absorption spectrometry (Vinas *et al.,* 1997). In Micro Analytical Center, Faculty of Science, Cairo University.

Initially, we will be talking about the most abundant element in honey, the potassium (Ramos *et al.,* 1999). When we look into table 1 as general view we see the concentration of potassium in honey samples are ranging from 253.6 to 4675.5 mg / kg with a mean of 1268 mg / kg. These results are compatible with the U.S. honey, which ranges from 100 gm/kg to 4700 mg/kg (Crane, 1979) and also with the Egyptian honey, which ranges from 215.0 mg/kg to 15550 mg/kg (Rashed and Slotan, 2004).

The second element which was measured in all honey samples except samples 9 and 11, was the sodium whose concentrations in honey samples are ranging from 41.0 to 588.0 mg / kg with a mean of 200.0 mg / kg. These results are compatible with U.S. honey, which ranges from 0.6 to 400 mg / kg (Crane, 1979) except the Arab Gulf region which ranges from 0.2 to 666.5 mg / kg (Kaakeh and Gadelhak, 2005). All our results were compatible with these honeys but they are less than range of Egyptian honeys (378.0 to 2550.0 mg / kg) (Rashed and Slotan, 2004), except samples 7 and 18 (380.0 to 600.0 mg/kg) respectively as shows in table 3.

The most element content in our study after potassium is calcium, which has been measured of all samples except sample 20. 220.0 mg / kg (Andres and terrab, 2004), except samples 9,14 and 15 which were lower than the range.

Some authors report that the order of element concentration in honey is in the order K > Mg > Na (Long, 1968). This arrangement is not compatible with our results which was in the order K > Ca > Na > Mg.

Iron is one of the essential elements present in large quantity after magnesium in our study. The range of iron concentration in honey samples is from 4.24 to 8.0 mg / kg with a mean of 6.463 mg / kg. These results are compatible with range of U.S. honey from 0.1 to 3.4 mg / kg (Crane, 1979), the Canary Island honeys which ranges from 1.9 to 52.5 mg / kg (Hernandez et al., 2005) and Romanian honey samples which range from 10.0 x10-4 to 10.0 mg / kg (Antonescu and Mateescu, 2019). All results are compatible with range of these honeys.

Zinc, one of element which has been measured of all honey samples. Its concentration in honey samples ranges from 1.13 to 7.83 mg /kg with a mean of 2.81 mg / kg. These results are compatible with U.S. honey, which ranges from 0.2 to 0.5 mg / kg (Crane, 1979), except for sample 15 (7.82 mg / kg) which was higher than the range. These results are compatible with Middle Anatolia honey (Turkey) which ranges from 1.1 to 24.2 mg / kg (Tuzen and Soylak, 2005).

Table 1. Locations of Sampling Relative to Benghazi City

Location classified relative to Benghazi City	Location / sample no.		Distance of road	Farness of houses	Farness of farms; others	Exposure to insecticides
Seaboard east or near to seaboards	Ras El-Helal	3	4 to 5 km	Few mountainous houses	No, mountainous climate	None
	Deryana	4 6	17 km	Absent	2 to 3 km	Available due to locusts by uses planes
	Al-Hamida	5	3 km highway road, also off-road uses by tractors	Houses inside the farms	3 km. wheat and barley farms and > 20 km fuel station	None, but may be affected by insecticides planes (cognate place)
	Sousa	13	Very near	Far away	No. mountainous climate	None
Mountainous or inboard east	Ben Qerdan	8	40Km	No houses are present	No farms are present	None
Mountainous or inboard east	Ben Qerdan	8	40 km	Absent (desert climate)	Absent	None
	Taknis	9	Absent	7 km	Absent	None
	Al-Abiar	10	3 km	Absent	Wheat and barley farms	None
	Al-Marj	11	Off-Road uses by tractors and cars	Houses inside the farms	Surrounding by seven farms	Available, for trees and vegetables
	Jurdas	14	Absent	7 km	Absent	None
	Wadi El-Koof	16	1.5 to 3 km	Small Village (near)	0.5 km Completely Surrounded by farms	Available, trees
		18	2.5 to 3 km	4 to 5 km medical village	No, but 10 to 12 km there is fuel station	None
inboard west	Msallata	2	5 km	Few houses	2.5 to 3 km and 30 km fuel station	None
	Qwarsha	7	< 1 km	Houses inside the farms	Wheat and barley farms, 0.5 km trash place, cement plant and 5 to 6 km sewage station	None
	Ajdaabia	12	17 km	Absent	Absent	No

		17	**Not estimated**	**1.25 km**	**No, but 1 km trash place and grazers bazaar**	**Available, for grazers**
Seaboard west	**Qasr El-Sharief**	**1**	**Off-road uses by tractors and cars**	**300m, three houses; 0.5 km medial village**	**3 km, wheat and barley farms and 20 km fuel station**	**None**
	Mesrata	**15**	**4 to 5 km**	**2 to 2.5 km, few**	**0.5 km from sea**	**None**
South Libya	**Tazerbo**	**19**	**2 km**	**1 to 3 km**	**Surrounding vegetables and palm trees farms**	**Available, for palm trees**
	Ubari	**20**	**2 km**	**Houses inside the farms**	**Serval farms, specially orange trees**	**None**

Table2. Botanical Source vs Geographical Origin of Libyan Honey samples

Sample no.	Location	Common name (Local name)	Scientific name
1	Qasr El-Sharief	Sedr	Ziziphus sp.
2	Masallata	Zaater	Thymus sp.
3	Ras El-Helal	Hannon	Arbutus sp.
4	Deryana	Qaamool	Cynara sp.
5	El-Hamida	Qaamool	Cynara sp.
6	Deryana	Rabea	Uncertain
7	Qwarsha	Kafoor	Eucalyptus sp.
8	Ben Qerdan	Sedr	Ziziphus sp.
9	Taknis	Zaater	Thymus sp.
10	Al-Abiar	Sedr and Zaater	Ziziphus sp. and Thymus sp.
11	Al-Marj	Rabea	Uncertain
12	Ajdabia	Al-Shokeyat	Uncertain
13	Sousa	Al-Mun	Honeydew
14	Jurdas	Inmeela	Marrbuim sp.
15	Mesrata	Ghasool	Mesembryanthemum sp.
16	Wadi El-Koof (1)	Kharrob	Ceratonia sp.
17	Ajdaabia	Kafoor	Eucalyptus sp.
18	Wadi El-Koof (2)	Kharrob	Ceratonia sp.
19	Tazerbo	Saphsafa	Medicago sp. (Alfalfa)
20	Ubari	Athel	Tamarix sp.

RESULTS AND DISCUSSION

The results of this work are summarized as follows:
To take in consideration, there are several parameters that influence the mineral content of honeys, such as temperature, humidity, soil and floral type, among others (Mendes *et al.*, 2013), therefore is not possible to make definitive conclusions about the mineral content of honey.

Table 3. Elements Content in Libyan honey samples

Sample no.	Element mg/kg Location	K	Ca	Na	Mg	Fe	Zn	Cu	Mn
1	Qasr El-Sharief	1125.5	455.0	98.5	15.75	7.50	1.75	1.05	1.55
2	Masallata	950.0	505.0	135.0	15.25	7.75	2.25	1.15	1.35
3	Ras El-Helal	1975.0	560.0	173.0	19.00	8.25	2.00	1.25	1.45
4	Deryana	1400.0	575.0	222.5	40.00	5.00	1.25	1.05	2.00
5	El-Hamida	1395.0	670.0	290.5	44.50	7.00	2.75	0.75	0.97
6	Deryana	960.5	375.0	109.0	22.00	4.95	0.50	1.50	1.75
7	Qwarsha	1305.5	575.5	666.0	45.50	8.05	3.95	0.55	1.25
8	Ben Qerdan	1375	500.0	110.5	21.75	7.00	2.05	0.75	1.00
9	Taknis	815.0	520.5	366.5	9.25	7.25	2.25	0.90	1.75
10	Al-Abiar	1580.0	340.0	207.5	26.00	5.75	1.75	1.00	0.90
11	Al-Marj	405.0	450.0	67.5	9.75	7.75	1.50	0.50.	1.75
12	Ejdaabia (1)	290.0	676.5	143.0	18.25	8.25	1.50	0.85	1.25
13	Sousa	1750.0	452.0	279.0	42.00	6.95	4.50	1.10	1.25
14	Jurdas	505.0	299.5	48.0	7.00	8.05	3.00	1.45	1.90
15	Mesrata	253.5	47.0	112.0	5.00	5.05	8.25	1.70	1.85
16	Wadi El-Koof (1)	695.0	595.0	196.0	42.00	8.95	3.95	0.90	0.85
17	Ejdaabia (2)	655.0	395.5	315.5	23.75	6.75	4.75	0.75	1.15
18	Wadi El-Koof (2)	1505.0	789.5	398.0	44.25	6.25	3.55	0.70	1.70
19	Tazerbo	4705.0	62.0	155.0	43.00	3.75	4.25	1.30	1.33
20	Ubari	1195.0	122.0	127.0	15.00	9.25	4.00	1.45	1.50
Range	-------------	253.5-4705.0	47.0-789.0	48-666.0	5.00-45.50	3.75-9.25	0.50-8.25	0.55-1.70	0.85-1.90
Mean	-------------	1242	448.25	182.45	25.45	6.975	2.9875	1.7975	1.425
Total	-------------	24840	8965	3649	509	139.5	59.75	35.95	28.5

The range of calcium concentration in honey samples is from 45.0 to 782.0 mg / kg with a mean of 455.0 mg / kg, as shows in table 1. These results are higher than the range of U.S. honey which is from 40.0 to 300.0 mg / kg (Crane, 1979), except samples 14,15 and 19 which were compatible with the range of Spain honey. All our results are also higher than those in honey collected from different regions (ranges from 47.0 to 132.0 mg/kg) (Lopez *et al.*, 1999), showing that all our results are higher than it, except sample 19 which was in the range and sample 15 which was lower than the range.

Magnesium in our results is one of the most abundance elements in honey after K, Ca, and Na as we will see.

Content of magnesium in honey samples as we show in table 1 are ranging from 7.0 to 43.0 mg / kg with a mean of 25.0 mg / kg. All these results are compatible with the U.S. honey, which is ranges from 7.0 to 130.0 mg / kg (Crane, 1979), Also, all our results are compatible with the Moroccan honey which is ranging from 10.0 to Copper concentration in honey samples ranges from 0.48 to 1.5 mg / kg with a mean of 0.99 mg / kg as we see in table 3. Some of these results are compatible with the U.S. honey which ranges from 0.01 to 0.1 mg / kg (Crane, 1979), but samples 3, 6, 13, 14, 15, 16, 19 and

20 are higher than the range. Also samples 1, 2 and 10 are slightly higher than this range. These results are compatible with England honey which has ranges from 0.035 to 6.51 mg / kg (Jones, 1987).

Finally, Manganese which was latest essential element has been measured. The concentration of manganese in honey samples ranges from 0.98 to 1.68 mg / kg with a mean of 1.32 mg / kg. These results are lower than U.S. honey, which ranges from 2 to 100 mg / kg (Crane, 1979). All our results are in the range of Chilean honey which ranges from 0.01 to 6.97 mg / kg (Fredes and Montenegro, 2015).

CONCLUSION:

All honey samples are containing different levels of these elements as will see, and is not possible to make definitive conclusions about causes of these elements, due to honey as a product of bees able to give evidences for the impact of environmental pollution within an area of around 7 km2, therefore we was collected some information from beekeepers about each sample under study to set some probabilities of presence of these element (see table no. 3). Also, when we analyzed all Libyan honey sample under study for some elements which are regarded as essential elements K, Na, Mg, Fe, Zn, Cu, and Mn, we concluded that all these elements are present in quantities compatible with several international honeys. Elements such as calcium in Libyan honey is present at high levels than those from several international honeys, which may distinguish the Libyan honey among them. Also we don`t note any elevated essential elements quantities that can cause harmful effects. Moreover, reports showed that the order of element concentrations in honey is in the order K > Mg > Na, but with respect to Libyan honey samples under study the order of essential elements of most these samples are: K > Ca > Na > Mg > Fe >Zn > Mn > Cu

Our results prove that the iron is an essential element in Libyan honey, due to its presence in moderate quantities in all samples although the difference in botanical sources and geographical origin of most samples. The Zinc concentration in all Libyan honey samples are compatible with several international honeys and usually was lower or slightly higher than other honeys. Finally, regarding manganese and copper, all samples contain small quantities of both elements.

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