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Measurement of Some Physical Properties of Libyan Honey

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Abstract

Twelve honey samples of ziziphus spina, thyme and multiflora types, were collected from a beekeeper from Zawia city (west of Libya). In this study, some physicochemical properties of the twelve honey samples were measured such as moisture content, specific gravity, electrical conductivity, total dissolved solids, pH value, and free acidity. The results indicated that the quality of Libyan honey samples was corresponding to the international standards. The average value of moisture content of the ziziphus spina honey was 9±0.7%, thyme honey 9.38±0.8 % and multiflora honey 10.73±1 %, the low moisture content protect honey from fermentation. The specific gravity ranged from 1.341 to 1.423 for all tested honey samples, which was inversely proportional to moisture content. The electrical conductivity of all honey samples was found within the international limits, with a maximum of 442±6 µS/cm, while total dissolved solids varied from 202 to 300 ppm. The pH ranged between 3.5 to 5.6, while the free acidity was between 10 to 20 meq/kg. According to the International legislation of honey; the examined honey samples have high quality and purity and are worth international specifications.

Key words: Honey, Honey quality, Physical parameters, Libya.

الملخص:

اثني عشر عينة من العسل الليبي من أصول نباتية مختلفة تتمثل في عسل السدر، عسل الزعتر وعسل الربيعي، تم جمعها من مربي نحل من مدينة الزاوية (غرب ليبيا). حيث

تم في هذه الدراسة قياس بعض الخواص الفيزيائية والكيميائية لهذه العينات، مثل محتوى الرطوبة، الكثافة النوعية، الموصلية الكهربائية، إجمالي المواد الصلبة الذائبة، قيمة الأس الهيدروجيني، والحموضة الحرة.
أظهرت نتائج هذه الدراسة أن جودة عينات العسل الليبي التي تم فحصها كانت مطابقة للمواصفات العالمية. حيث بلغ متوسط محتوى الرطوبة لعسل السدر(9±0.7%) وعسل الزعتر (9.38±0.8%) والعسل الربيعي(10.73±1%) ، حيث انخفاض محتوى الرطوبة يحمي العسل من التخمر، وتراوحت الكثافة النسبية من 1.341 إلى 1.423 لجميع عينات العسل المختبرة، والتي تتناسب عكسياً مع محتوى الرطوبة. كانت الموصلية الكهربائية للعينات ضمن الحدود الدولية وسجلت 442±6µS/cm كحد أقصى، وتراوحت قيمة المواد الصلبة الدائبة الكلية من 202ppm إلى 300 ppm بينما تراوح الأس الهيدروجين بين 3.5 إلى 5.6 والحموضة الحرة تراوحت من 10 meq/kg إلى 20 meq/kg. وفقا لتوصيات المفوضية الأوربية والتشريعات الدولية للعسل، تتمتع عينات العسل المختبرة بدرجة عالية من النقاء والجودة، فهي مطابقة للمواصفات الدولية.

1. Introduction

Bee honey is a natural, sweet, viscous fluid produced by honey bees (*Apis mellifera*) from the nectar of plants or from secretions of living parts of plants, which the bees collect, transform by combining, depositing, dehydrating, storing and leave in honeycombs to ripen and mature [1,2]. Bee honey composition and characteristics depend on several factors. The most important factor is the flower types that provided the nectar source. Other factors that play a crucial role in honey quality including: geographical floral origin, season and climatic condition during productions, storage conditions, and treatment of beekeepers [3-7]. Bee honey is one of the few totally foods that the body easily assimilated, it consists of nutrients that provides source of energy, especially high-energy carbohydrate food [8]. There are more than 22 types of sugar in the honey in which of that Fructose and Glucose constitutes the highest content, and they are easily digestible as those in many fruits [7]. The fructose/glucose ratio indicates the ability of honey to crystallize [8]. Council Directive of European Union reported the criteria of

total glucose and fructose content should be no less than 60 g/100 g for nectar honey. Sucrose content should be no more than 5 g/100g. Honey also contains amino acids, enzymes, vitamins, minerals, proteins, organic acids and phenol compounds [1, 9].

As known, honey is a natural product, having a high nutritional value besides to its therapeutic effectiveness, as it possesses antiviral, antioxidant, antimicrobial, and anti-inflammatory properties, as well as a wound healing activity [10]. The healing property of honey is due to the fact that it provides antibacterial activity, and its high viscosity helps to provide a protective barrier to prevent infection [10-12]. Several scientific reports confirmed that honey has important biochemical therapeutic activities [13]. In order for honey to have a beneficial effect on human health and be useable for therapy, honey should be of high quality and free of contaminations, such as toxic heavy metals which exceed the permitted levels, and other risks to human health [14,15]. To verify that honey is of high quality, and free of contamination, as well as suitable for medicinal usage, honey must undergo several tests to determine the physicochemical and microbiological properties of honey [16].

Libyan people use a honey for traditional therapeutic purposes and as a nutritional supplement. However, few data have been published investigated the physicochemical properties of eucalyptus honey [17]. Ahmida *et al.* (2010) examined the physicochemical characteristics of different Libyan honey samples, which were collected from Benghazi city and found that the electrical conductivity ranged from 0.29 to 0.74 mS/cm, the specific gravity ranged from 1.2081 to 1.2270, pH values ranged from 3.56 - 4.99 and moisture content ranged from 13.3% to 17.2% [18]. Awad *et al.* (2016), studied honey samples collected from Kasr Khiar and Garaboli area, west of Libya, and recorded the average value of moisture, pH, specific conductivity, total dissolved solids, specific gravity, and the acid equivalent of 18.722 %, 3.77, 587.8µS / cm, 674 ppm, 1.368, and 23.33 m Eq./ kg respectively for Kasr Khiar

samples, while for Garaboli samples the average values for the same parameters were found to be 18.11 %, 4.09, 777 µS / cm, 1255 ppm, 1.38, and 16.66 m Eq./ kg respectively [16]. Salama *et al.* (2019) conducted a study on honey samples collected from different locations in the west of Libya, the results showed that the mean values of moisture ranged from 20.6 to 25.1% which is considerably high and it could be due to the honey immaturity or humidity of its source. pH mean values 4.12 to 4.74, free acid equivalent 20 to 27 m eq./kg, total dissolved substance 646 to 994 ppm, and specific conductivity 638.5 to 1004 µS/cm [19]. Generally, data obtained from the mentioned studies indicated that the quality of honey samples ranged with the International specifications. However, many studies accomplished all over the world to investigate the physicochemical properties of bee honey in order to determine its quality and purity.

1.1. The aim of study

Physicochemical properties prove to be the most important parameters in assessing the quality and acceptability of bee honey. The purpose of this study was to estimate some physicochemical properties of honey samples collected from Zawia city, Libya, including moisture content, specific density, electrical conductivity, total dissolved solids, pH and Free acidity.

2. Materials and Methods

2.1. Honey samples

Twelve botanical honey samples of three types of honey (four samples for each honey type), were collected from a honey beekeeper in Zawia, Northwest Libya, representing Ziziphus Spina, Thyme and Multiflora honey. The local names of these honey types are Sider, Elzaater, Al-Rabii honey respectively. Ziziphus Spina and thyme honey types were produced in the summer season, as two samples of each type were collected in July 2020, and the others were in June 2021. While the multiflora honey type was produced in the spring season, two samples of this type were collected in April 2020 and the others were in April 2021. The samples were kept in

glass jars and stored at room temperature away from direct sunlight until analyzed.

2.2. Sample preparation for physicochemical analyse

The experimentations of physicochemical properties assessment were conducted in the physics and chemistry laboratory of the Specific Training Center for Oil Industries, Zawia, Libya, analyzed between December 2021and February 2022. The honey solutions were prepared immediately before the tests, which were stirred using a magnetic stirrer. And the method of preparing honey solutions was performed as follows:

2.2.1. Moisture content: The moisture content was assessed by the oven-drying method according to the method cited by [20]. Measuring 2 g of each sample and put in a dish and dried in the oven at 110 °C for 2 hrs, covered, cooled in a desiccator, and weighed. The sample was re-dried for one hour in the oven, cooled and reweighed. The process was repeated at one-hour intervals until a constant weight was obtained. The percentage moisture was calculated using the following equation:

$$\text{Moisture content} = \frac{W_1 - W_2}{W_1 - W_0} \times 100 \quad (1)$$

Where: W_0 = Weight of dish (g)
W_1 = Weight of the fresh sample + dish (g)
W_2 = Weight of the dried sample + dish (g)

2.2.2. Measurement of specific gravity: The specific gravity of honey was evaluated by dividing the weight of a certain volume of honey sample by the weight of the same volume of distilled water at a certain temperature, 10 ml of each honey sample was weighed using a sensitive balance and compared to the same volume of distilled water, according to the method described by [9,15], then the specific gravity was calculated by the following formula [21]:

$$SG = \frac{W_{honey}}{W_{water}} \quad \text{(A dimensionless quantity)} \quad (2)$$

2.2.3. Measurement of Electrical conductivity &Total dissolved solids: EC & TDS of honey samples were measured using (Hanna instrument HI 2300 EC/TDS/NaCl meter). A honey solution of 20 g honey in 100 mL of distilled water (20% w/v) at 25 °C, according to the methods proposed by [22, 23].

2.2.4. Determination of pH and Free Acidity: pH was measured using pH meter model 80. A solution containing 10 g of honey was dissolved in 75 mL distilled water, and the pH was read. Then the same solution was titrated with 0.1 mol NaOH solution until pH value reach 8.3, that Free acidity in (meq kg^{-1}) was calculated as follows:

$$\text{F.A (meq kg}^{-1}) = \frac{\text{volume of 0.1M NaOH (ml) consumed} \times 10}{\text{kg of honey sample}} \qquad (3)$$

Where 10 signifies the dilution factor of the honey sample during analysis, based on the procedure cited by [23-25].

2.3. Statistical analysis

The readings were carried out in triplicates and showed as the range of values, the average ± standard deviation. The statistical analyses of the results were done by Microsoft Office Excel 2016.

3. Results and Discussion

The findings of tested physicochemical parameters of Libyan honey samples are listed in Table 1.

Table 1. physical parameters of tested Libyan honey

Honey types	Parameters					
	MC (%)	SG	EC (µS/cm)	TDS (ppm)	pH	FA (meq/kg)
Ziziphus Spina						
Range	8-9.8	1.359-1.423	434-450	260-300	4.3-5.6	10-17
mean±SD	9±0.7	1.405±0.03	442±6	272±18	5.05±0.5	13±3.3
Thyme						

Range	**8.510.34**	**1.371-1.412**	**363-449**	**218-268**	**4.2-5.1**	**15-20**
mean±SD	**9.38±0.8**	**1.401±0.02**	**385±42**	**230.5±25**	**4.8±0.4**	**18±2**
Multiflora						
Range	**9.5-11.9**	**1.341-1.382**	**336-370**	**202-219**	**3.5-5**	**15-20**
mean±SD	**10.73±1**	**1.354±0.01**	**357±15**	**212±7**	**3.9±0.6**	**18.75±2.5**
European criteria	**≤ 20**	**1.38-1.45**	**≤ 800**	**-**	**3.2-4.5**	**≤ 50**

MC; moisture content. SG; specific gravity. EC; electrical conductivity. TDS; total dissolved solids. FA; free acidity.

3.1. Moisture Content (MC): As shown in Table 1 the mean value of MC of honey samples was 9±0.7 % for Ziziphus Spina samples, 9.38±0.8 % for thyme samples, and 10.73±1 % for multiflora samples, this result of MC was within the European Standard legislation and Codex Alimentarius Standards. The current results are lower than those reported by [16] who reported the MC of 18.72% and 18.11% of honey samples collected from Kasr Khiar and Garaboli, west of Libya. [19] also reported MC values of honey samples from west Libya, which ranged from 20% to 25.1%, which is higher than the current result. Moreover, our results were close to those obtained by [15] who studied honey samples from Misurata, western Libya, and found that the MC is ranged from 4.74% to 7.7%.

The MC of honey is related to the environmental conditions, climatic factors, the harvest season and the maturity degree. The results showed that the Ziziphus Spina and thyme honey samples have low MC, which is due to the harvest season, where these types of honey are produced in the summer season. Increasing MC of honey causes honey fermentation, so the low MC protects honey from the microbiological activity and thus honey can be stored for longer periods, therefore reducing the moisture content of honey retard the fermentation process [26].

3.2. Specific Gravity (SG): The typical SG value of honey ranges from 1.38 to 1.45 at 20 ºC [27]. In this study, the average SG was 1.354±0.01 for multiflora honey, 1.401±0.02 for thyme honey, and 1.405±0.03 for Ziziphus Spina honey, which is in accordance with the standard limits. [16] recorded results of SG with average values of 1.36 and 1.38 for the Kasr Khiar and Garaboli areas, which is in agree with recent results. In contrast, [18] who studied honey samples collected from Benghazi, east Libya, reported SG values within the range of 1.2081 to 1.2270, which is lower than the standard recommendations. From the experimental data, noticed that a negative correlation (R=0.99, P=0.2%) exists between MC and the SG of honey, as shown in figure 1, which has also been observed by [6,9,20]. Multiflora honey sample with MC of 10.73% has the lowest SG value of 1.354. Ziziphus Spina and Thyme samples with MC of 9%, 9.38% did not have a difference in SG. The higher MC of honey the lower its SG. MC and SG are used as a measure of adulteration in honey, where the density depends on the chemical composition of the substance.

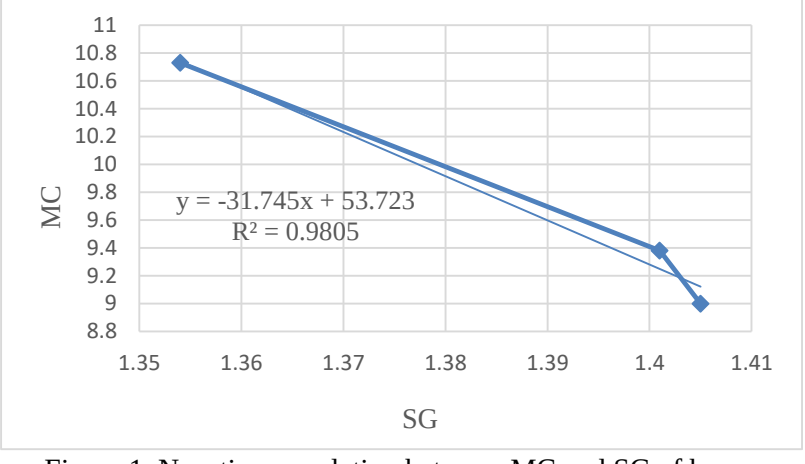

Figure 1. Negative correlation between MC and SG of honey

3.3. The electrical conductivity (EC): According to Council Directive, the EC value should be not more than 0.8 mS/cm = 800 µS/cm. In the present study, the honey samples were within the

European criteria and The International Honey Commission. This point out all honey samples are from nectar honey, which has a lower conductivity than honeydew honey. The Ziziphus Spina honey samples showed the highest EC average 442±6 µS/cm, 385±42 µS/cm for the thyme honey samples, and 357±15 µS/cm was the lowest EC average for the multiflora honey samples. The EC values of this study were lower than the values reported by [16] in a previous study of honey samples from the West of Libya, which ranged from 582 to 792 µS/cm. The result of thyme honey EC in the current study is in agreement with the result of [28] who reported the average EC in Greece thyme honey (420±0.08) µS/cm. Whereas [29] and [30] published an average value of about (650 µS/cm) for EC of Algerian and Moroccan Ziziphus honey which is higher than the results obtained by the recent study. In general, the EC depends on the concentration of mineral salts, organic acids, and botanical origin of honey [31,32], and it can be considered as a reliable criterion for the differentiation of the botanical origin of bee honey, also determines the purity and quality control of honey [25].

3.4. Total dissolved solids: TDS was measured as the content of organic and inorganic ionic substances dissolved in honey [16,19]. The TDS has the lowest average of 212±7 ppm in the multiflora honey samples, then increased in the thyme samples to 230.5±25 ppm, to reach 272±18 ppm in the Ziziphus Spina samples. These findings are less than that obtained by [16] and [19], who reported (674-1256 ppm) and (646 to 996 ppm) respectively, for honey samples collected from west of Libya. A study conducted in Romania showed TDS value ranging from 77.8-81.07 ppm [33].
The results reveal a significant correlation (R=0.99, P=0.1%) between TDS and EC, as illustrated in figure 2, which indicates that both parameters can be used to estimate honey quality and purity. Noticeably, TDS is mostly affected by MC, as the increased MC will decreases the TDS values. Multiflora honey samples with a MC of 10.73% had the lowest TDS, the Ziziphus Spina honey sample has a MC of 9% and the highest TDS. Where decreasing the moisture content can conserve the quality of honey.

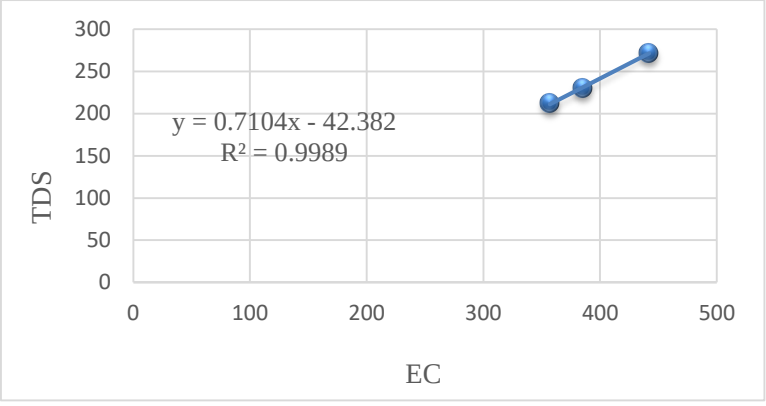

Figure 2. Correlation between TDS and EC of honey

3.5. pH and Free acidity: The studied honey samples are found to be acidic, with pH values ranging from 3.5 to 5.6. Ziziphus Spina honey samples recorded the highest pH value, with an average of 5.05±0.5, that of thyme honey samples was 4.8±0.4, and that of multiflora honey samples was 3.9±0.6. These results are in agreement with the range of the established Codex standard of honey, varying from 3.6 to 5.6 [34]. The pH values reported in the present study are also in the same range found by researchers [29,35-39], which ranged from 3.3 to 5.9. The difference in pH values may be due to the variation of different acids and minerals present in honey [37,39].

The free acidity of all samples was low. An average value of 13±3.3 meq/kg was obtained in Ziziphus Spina honey samples, 18±2 meq/kg for the thyme honey samples, and 18.75±2.5 meq/kg for the multiflora honey samples, the average acidity value of multiflora honey samples in this study was similar to that of Polish multiflora honey [6]. All tested honey samples have Free acidity below 50 meq/kg, these values indicated that the samples are free of any fermentation.

As the pH value is the negative logarithm of hydrogen ion concentration, the free acidity is the sum of all free acids present in honey [40]. All honey is naturally acidic due to the presence of organic acids, where gluconic acid is the main acid, in addition to other acids in smaller amounts, this acidity of honey helps to prevent

the fermentation by microorganisms [41,42], as most microorganisms grow best at pH values around 7 [37].

4. Conclusion:

Results obtained from this study showed that the three-studied honey types have good physicochemical characteristics and agree with the international standard limits, and the botanical origin of honey samples was clear in the electrical conductivity values. The examination result of acidity confirmed, that the honey samples possess high acidity, which indicates the capacity of honey to inhibit the bacteria and other microorganisms to grow. Low moisture content also denotes the honey's ability to resist spoilage caused by fermentation. Based on the findings, the investigated physicochemical parameters of the three honey types didn't exceed the International standards.

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