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CHEMICAL AND PHYSICAL PROPERTIES OF SOME EGYPTIAN AND LIBYAN HONEYS

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ABSTRACT

Six different types of Egyptian honeys (Citrus, Clover, and Cotton) and Libyan honeys (Rabeay, Sidir and Thymus) were collected from different regions and studied. The aim of the present work was to describe honeys, in order to contribute to their characterization for commercial purposes. Samples were physicochemical and sensory examined using a quantitative descriptive analysis method. It could be concluded that Libyan honeys had the highest viscosity values than the Egyptian honeys.

It is not surprising that potassium (K^+) was quantitavely the most important mineral present higher values of 1934.7 ppm. Meanwhile, manganese was the inferior of all honey types ranged from (1-1.5 ppm) in citrus and thymus honeys, respectively. Sidir honey from Wady El Hay was outstanding superior for the contents of Mn (5 ppm) than all the other tested honeys. Citrus honey was the inferior from all of the others honeys for Ca, Mg, Na, K, Fe and Mn. Proline the most important from a quantitative point of view was followed by Aspartic amino acids. Sidir honey has the highest values of NH4. Thymus honey has the highest number of total amino acids of all samples followed by Cotton honey represented by 6.080 and 4.920 mg/g., respectively. Whereas, Rabeay honey was the least in total amino acids, represented by 0.488 mg/g. Thymus and Citrus honeys contain the largest number of amino acids of all honeys but thymus was superior to citrus honey in quantities of amino acids existing. Honeys were correctly classified according to its floral origin. Further studies are needed in order to investigate other floral origins to provide a robust model to classify honey samples from this region.

Keywords: Honey analysis, amino acids, minerals, physical characters, geographical origin.

INTRODUCTION

Honey is the sweet substance produced by honey bee from the flowers or from the secretions of living parts of plants, which they collected, transform, combine with specific substances or extraction of plant sucking insect on the living parts of plants, which honeybee collect, transformed combine with specific substances of their own, store and leave in the honey comb to ripen and mature. This is the general definition of honey in the (Codex Alimentarius, 1998). Chemically, honey is quite complex. It comprised primarily sugars; however, it contains many other potentially biologically active components, such as antioxidants, which display antimutagenic activity (Wang *et al.,* 2002).

Honey composition is tightly associated to its botanical origin, which is closely related to the geographical area in which it is originated, because soil and climate characteristics determine melliferous flora as well as the presence of different minerals arising from soil, dust, etc. (Nelly *et al*., 2005). The floral origin of honey is an important characteristic in the evaluation of its quality (Baroni *et al*., 2006). Products from one region may attain a surplus value than similar products from another area. However, labeling of regional honey must be supported by analysis that confirms its provenance (Gonlez Params *et al*., 2000; Woodcock *et al*., 2007).

Mineral composition has also been employed to discriminate honey arising from different geographical areas. Minerals seem to be good candidates for a classification system, mainly because they are stable and can be associated to the soil where melliferous flora grows (Anklam, 1998). Among the parameters tested to assess the provenance of honey, electric conductivity, acidity, amino acids, carbohydrate profile and pollen proteins were found to be the most useful (Popek, 2002; Baroni *et al*., 2002; Baroni *et al*., 2004; Nozal *et al*., 2005; Cometto *et al*, 2006). The quality and biochemical properties of honey were related to honey maturity, production methods, climatic conditions, processing and storage conditions as well as the nectar source of honey.

The main goal of this work was to characterize honey produced in two countries, Egypt and Libya, establishing associations among chemical variables and the production zone. Thus, several physical and chemical parameters, including minerals and amino acids were evaluated. The objective of this work is to identify the variables that discriminate honey arising from both regions of Egypt and Libya.

MATERIALS AND METHODS

The present investigation was carried out at National Research Centre, Central Labs, Dokki, Giza, Egypt during 2011, to study chemical and physical properties of the Egyptian and Libyan honeys which collected from different sources and different regions. Six samples of honeys represented the three main Egyptian and Libyan honeys were collected from different location in Egypt and Libya, these regions were:

1- North Egypt which represented, Sharkia, Qalyubia and Dakahlia governorates.
2- West- North Libya which included by Al-Sarag, El-Khoms and Wady El-Hay governorates. Table (1)

Table (1): Egyptian and Libyan honey types and their plant sources.

No.	Honey types	English name	Region	Plant sources (Scientific name)
1	Egyptian honeys	Citrus	Benha- Qalyubia	*Citrus spp.*
2		Clover	Manzala- Dakahlia	*Trifollium alexandrinum*
3		Cotton	Belbees- Sharkia	*Gossypium barbadence*
4	Libyan honeys	Rabeay	Al Sarag- (20 Km.)West Tripoli	*Citrus+ multiflorum*
5		Sidir	Wady El Hay- (80 Km.) South Tripoli	*Ziziphus spina-christi*
6		Thymus	El Khoms- (80 Km.) East Tripoli	*Thymus vulgaris*

Samples were collected in light plastic jars kept in freezing conditions until analyses.

All samples were analyzed for the following properties:

Samples of honeys were prepared for chemical analysis according to Cottenie *et al*., (1982). 1. Primary, secondary moisture and ash content were determined according to A.O.A.C. (1995). 2. Potassium, sodium and calcium were determined by flame photometer apparatus. 3. Microelements (Fe, Mg and Mn) were determined by Atomic Absorption 157 (International Labs). 4. Nitrogen was determined using Microkjeldahl method.

RESULTS AND DISSCUSSION

Relationship between geographical origin of production honey and physical, amino acids and minerals was illustrated in Tab.(2-6) and Fig. (1-6).

Physical properties:

As shown in Table (2) shows the some physical properties according to study countries (Egypt/Libya). Moisture, a parameter that is related to the climatic conditions and the degree of maturity, showed values minimum than 18%. None of the samples exceeded the 20% allowed by (Codex Alimentarius, 1993).

Table (2): Some physical properties of Egyptian and Libyan honeys

	RPM	10	20	40	60	80	100	150	200
Citrus Honey	S.S	259	430	781	-	-	-	-	-
	S.R	2.2	4.4	8.8	-	-	-	-	-
	Visco. Cp	11566	9814	8830	-	-	-	-	-
	Torque %	24.2	40.5	73.9	-	-	-	-	-
Clover Honey	RPM	10	20	40	60	80	100	150	200
	S.S	317	555	1045	-	-	-	-	-
	S.R	2.2	4.4	8.8	-	-	-	-	-
	Visco. Cp	14301	12645	11925	-	-	-	-	-
	Torque %	29.9	52.3	99.8	-	-	-	-	-
Cotton Honey	RPM	10	20	40	60	80	100	150	200
	S.S	134	209	348	489	630	768	-	-
	S.R	2.2	4.4	8.8	13.2	17.6	22.0	-	-
	Visco. Cp	6143	4751	3959	3703	3569	3489	-	-
	Torque %	12.8	19.9	33.0	46.3	59.7	72.5	-	-
Sidir Honey	RPM	10	20	40	60	80	100	150	200
	S.S D/cm^2	663	-	-	-	-	-	-	-
	S.R/sec	2.2	-	-	-	-	-	-	-
	Visco. Cp	**30186**	-	-	-	-	-	-	-
	Torque %	62.5	-	-	-	-	-	-	-
Thymus Honey	RPM	10	20	40	60	80	100	150	200
	S.S D/cm^2	351	632	-	-	-	-	-	-
	S.R/sec	2.2	4.4	-	-	-	-	-	-
	Visco. Cp	**15933**	14373	-	-	-	-	-	-
	Torque %	33.2	59.7	-	-	-	-	-	-
Rabeay Honey	RPM	10	20	40	60	80	100	150	200
	S.S D/cm^2	455	853	-	-	-	-	-	-
	S.R/sec	2.2	4.4	-	-	-	-	-	-
	Visco. Cp	**20828**	19412	-	-	-	-	-	-
	Torque %	43.0	80.9	-	-	-	-	-	-

S.S: Shear Strength S.R: Shear Rate Visco. : Viscosity Programmable Rheometer
R.P.M: Round per minute Apparatus: Spindle 25, Brook Field, Model DV- 111

For physical characters table (2) demonstrated that Sidir honey has the highest values of viscosity of all tested honeys (30186 Cp.). Whereas, cotton honey was the inferior in viscosity values (6143 Cp.). It could be concluded that Libyan honeys (Sidir, rabeay and thymus) had the highest viscosity values than the Egyptian honeys (clover, citrus and cotton), respectively. This fact may be due to Libya is a desert country with high temperature and low relative humidity. As mentioned in Table (3) samples from Egypt and Libya presented different values for ash content, which could be attributed to different weather conditions, soil characteristics and/or floral origins. The wide variability of honey composition is reflected also in ash contents.

Table (3): Ash and humidity percentages from different Egyptian and Libyan honeys

Honey Types		Humidity Percentage (%)			Ash (%)
		Primary	Secondary	Total	
Egyptian honey	Citrus	8.78	1.16	9.84	0.03
	Clover	7.58	1.19	8.68	0.04
	Cotton	11.82	1.19	12.87	0.17
Libyan honey	Rabeay	6.47	1.22	7.61	0.07
	Sidir	4.74	1.15	5.84	0.26
	Thymus	6.67	1.16	7.75	0.08

This parameter that is usually used to classify honey (floral, mixed or honeydew honey) and is mainly determined by soil and climatic characteristics, showed values between 0.03 and 0.26%. All honeys analyzed in this work had ash contents below 0.6%, indicating that they were more likely to be of floral than honeydew origin. (Codex, 1993). Data showed that citrus honey has the inferior percentages of ash produced 0.03%. while, Sidir honey has the superior percentage of ash followed by cotton honey produced (0.26 and 0.17%, respectively). From Table (3) it could be concluded that Sidir honey has the least total humidity percentages as 5.84%. But, total humidity percentages in cotton honey were the highest (12.87%).

Minerals content:

Apart from the nutritional significance of minerals and the fact that they affect color of honey, mineral content is also an important indicator of possible environmental pollution and a potential indicator of geographical origin of honey (Downey *et al*., 2005).

Table (4): Minerals content of some Egyptian and Libyan honeys.

Honey types		Mineral elements					
		Cations (ppm)				Micro. (ppm)	
		Ca^{++}	Mg^{++}	Na^{+}	K^{+}	Fe	Mn
Egyptian Honeys	Citrus	100	24	108.7	554.0	3.75	1.0
	Clover	80	96	172.0	945.0	8.75	2.0
	Cotton	560	72	380.0	1934.7	7.50	2.0
Libyan Honeys	Rabeay	480	48	340.0	972.0	10.0	2.0
	Seder	120	24	340.0	829.4	5.00	5.0
	Thymus	140	24	186.0	944.0	3.75	1.5

Data illustrated in table (4) showed the chemical analysis of some mineral elements in some of the most important Egyptian and Libyan Honeys. It is not surprising that potassium (K^+) was quantitavely the most important mineral present higher values of 1934.7 ppm. Meanwhile, manganese was the inferior of all honey types ranged from (1-1.5 ppm) in citrus and thymus honeys, respectively. These results are in agreement with these obtained by Terrab *et al*., (2004). They found that potassium (K^+) mineral has an average content of 679ppm followed by sodium and calcium. The highest value of potassium was observed in cotton honey present 1934.7ppm, followed by calcium, sodium and magnesium with values (560, 380 and 72ppm, respectively). Magnesium (Mg^+) was quantitavely the inferior of citrus, Sidir and thymus honeys presented by 24ppm for each. Rabeay honey has the highest quantitative content of Fe^{++} of all honey types present (10ppm) followed by clover and cotton honeys represented by 8.75 and 7.5ppm, respectively. While citrus honey was the inferior from all of the others honeys for Ca, Mg, Na, K, Fe and Mn presents (100, 24, 108.7, 554, 3.75 and 1.0 ppm), respectively.

Clover honey was superior in Mg contents presents 96 ppm, meanwhile cotton honey was the second for Mg contents (72 ppm). As mentioned in table (4) it obviously that Sidir honey from Wady El Hay, 80 Km. from Tripoli, Libya was outstanding superior for the contents of Mn (5 ppm) than all the other tested honeys. But it was inferior in Mg (24 ppm). In general, it can be conSidired that the presence of these metals is indication of contamination during processing, shipping or storage due to the use of steel or galvanised containers (Corbella and Cozzolino, 2006).

Amino acids content:

Data tabulated in table (5) and Figs (1-6) illustrated the amino acids existing in Egyptian and Libyan honeys. It could be concluded that, different amino acids can be found in honey, being Proline the most important from a quantitative point of view followed by Aspartic amino acids. Some authors report that high values of proline are typical for honeydew honeys. Proline can be used to distinguish genuine honey samples from honey produced from non floral sources (Guler *et al*., 2007).

Therefore, Thymus honey has the highest number of total amino acids of all samples followed by Cotton honey represented by 6.080 and 4.920 mg/g., respectively. Whereas, Rabeay honey was the least in total amino acids, represented by 0.488 mg/g. Thymus and Citrus honeys contain the largest number of amino acids of all honeys but thymus was superior to citrus honey in quantities of amino acids existing.

Table (5): Amino acids existed in Egyptian and Libyan honeys (milligram/gram)

Amino acids	Honey Types					
	Citrus	**Clover**	**Cotton**	**Rabeay**	**Sidir**	**Thymus**
Aspartic	0.217	0.046	0.215	0.133	0.218	0.163
Theronine	0.019	0.00	0.00	0.00	0.00	0.013
Seine	0.066	0.00	0.00	0.055	0.00	0.160
Glitamic acid	0.203	0.00	0.00	0.208	0.00	0.197
Glycine	0.032	0.00	0.00	0.019	0.00	0.024
Alanine	0.085	0.00	0.00	0.088	0.00	0.111
Valine	0.027	0.00	0.367	0.048	0.00	0.585
Isoleucine	0.023	0.00	0.00	0.00	0.00	0.00
Leucine	0.060	0.00	0.00	0.053	0.00	0.046
Tyrosine	0.00	0.00	0.00	0.00	0.491	0.526
Phenyalanine	0.00	0.00	0.00	0.00	0.00	0.290
Histadine	0.112	0.00	0.00	0.00	0.00	0.00
Lysine	0.077	0.00	1.516	0.00	0.00	0.079
Arginine	0.00	0.010	0.00	0.00	0.00	0.00
Proline	1.564	2.224	0.866	0.435	2.104	3.886
NH4	1.399	1.099	0.00	1.513	4.445	1.704
Total	2.485	2.293	4.926	0.488	2.814	6.080

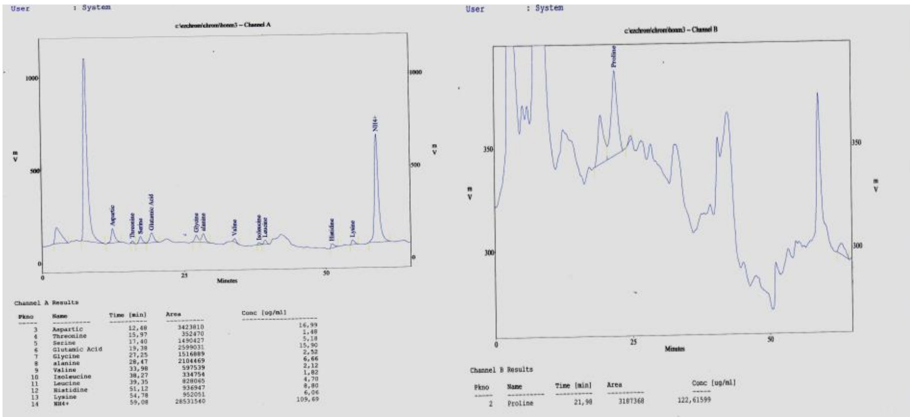

Figure (1): Amino acids in Citrus honey

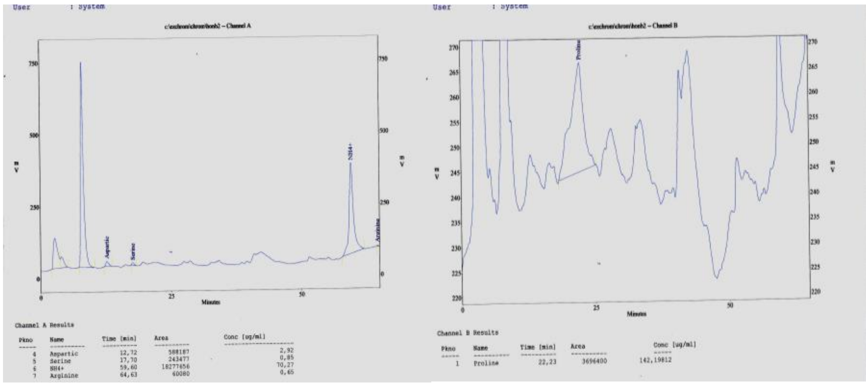

Figure (2): Amino acids in Clover honey

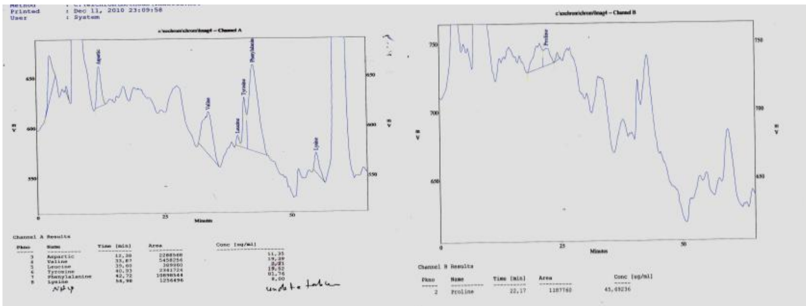

Figure (3). Amino acids in cotton honey

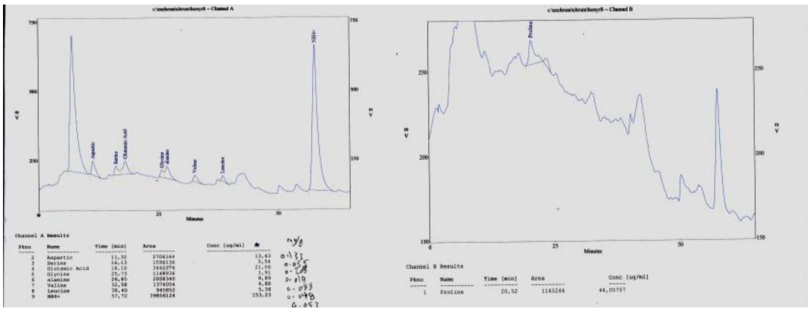

Figure (4). Amino acids in Rabeay honey

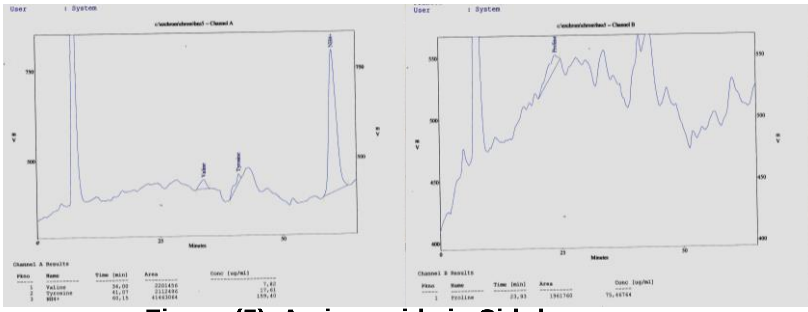

Figure (5). Amino acids in Sidr honey

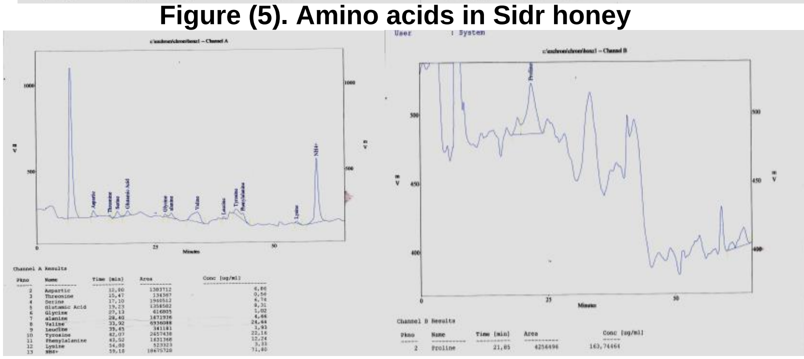

Figure (6). Amino acids in Thymus honey

Nine amino acids were not found in Clover, Cotton and Sidir honeys. These amino acids are Theronine, Seine, Glitamic acid, Alanine, Phenylalanine, Leucine, Isoleucine, Histadine and Glycine. Table (5) showed that each of Isoleucine and Histadine amino acids was not found except in Citrus honey of all tested honey samples represented by (0.023&0.112 mg/g), respectively. But Phenylalanine was not found except in thymus honey (0.290 mg/g). Meanwhile, Arginine was found only in Clover honey (0.010 mg/g). Regarding the free amino acids, expressed as amino nitrogen, showed results similar to previously published for Spanish honey. Amino acids have been previously used as indicators of botanical and geographical origin of honey (Iglesias *et al*., 2004 and Perez, *et al*., 2007). As shown in table (5) NH_4 was existed in all honey samples except in Cotton honey. Sidir honey has the highest values of NH_4, represented by 4.445 mg/g. Meanwhile, Sidir honey has only three amino acids, Proline, Tyrosine and Aspartic represented by 2.104, 0.491 and 0.218 mg/g, respectively. These results may probable due to differences between apiarian floras.

Finally, the evaluation of chemical profile, including analysis of minerals and amino acids (chemical traceability of honey) should enable to enhance the international trade, improving the trust of consumers to certified regional products, and ensuring its provenance to consumers. In our case, the evaluation of minerals as well as amino acids content in honey clearly reflect differences between both studied areas, triggering the need of comparing values of metal contents of honey from other geographical origin (worldwide) to fully establish the usefulness of the analysis of trace contents in the evaluation of honey provenance. Thus, the previous results indicated that honey produced in Egypt and Libya has remarkable quality.

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الخصائص الكيميائية و الطبيعية لبعض الاعسال المصرية و الليبية

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تم تحليل بعض الصفات الطبيعية و الكيميائية لكل من الاعسال المصرية (الموالح، البرسيم، القطن) و الليبية (الربيعى، السدر، الزعتر) الاحادية المصدر، و المجموعة من مناطق جغرافية مختلفة. تميزت الاعسال الليبية بدرجة عالية جدا من اللزوجه مقارنة بالاعسال المصرية. وجد ان عنصر البوتاسيوم (K^+) كان الاكثر تواجدا من بين العناصر الستة التى تم تقديرها وذلك فى عسل القطن، بينما كان عنصر الماغنيسيوم الاقل تواجدا من بين العناصر فى الاعسال المختبرة فى عسل الموالح و الزعتر. بالنسبة للاحماض الامينية، وجد ان الحمضين الامينيين البرولين و الاسبارتيك هما الاكثر تواجدا فى كل الاعسال المختبرة. احتوى عسل الزعتر الليبى على اعلى قيمة من الاحماض الامينية الكلية و يليه عسل القطن المصرى. بينما كان عسل الربيعى الليبى الاقل فى محتواه من الأحماض الامينية الكلية.

قام بتحكيم البحث

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أ.د / حمدى طاهر ابو العينين	**مركز البحوث الزراعية**