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Characterization of volatile compounds in floral honey from coriander using Gas Chromatography-Mass Spectroscopy

I. U. Khan[1], W. Dubey[1], V. Gupta[2]

[1]School of Science, JECRC University, Jaipur-303905, Rajasthan, India

[2]Agricultural Research Station, Ummedganj, (Agriculture University Kota) Rajasthan, India

Abstract

Honey has a long history of being used for human consumption and is used in various foods and beverages as a sweetener and flavouring agent. Flavor of honey varies based on the nectar source. Flavor/fragrance qualities of honey are very much dependent on the volatile and semi-volatile organic compounds present. GC-MS analysis of unifloral honey samples from coriander (*Coriandrum Sativum* L.) processed by *Apis melifera* was carried out on Shimadzu GCMS-QP2010 Ultra system. The identification of the chemical compounds was confirmed based through the peak area, retention time and matching of molecular formulas with data available on National Institute for Standards and Technology (NIST) mass spectral library, ver. NIST 11. 27 volatile compounds were detected. Sugar and hydrocarbons constituted 60% of the composition of coriander honey. Other classes of chemical compounds detected included acids, aldehydes, alcohols, ketones and furans.

Key words : *Apis melifera*, coriander,GC-MS, honey

Introduction

Honey has been used by *Homo-sapiens* from millions of years for nutrition and medicinal purposes. It is a solution of sugars containing secondary plant metabolites. Several reports have shown that the sugars and secondary metabolites are varying depending on the source and botanical origin of the nectar. Several literatures reported that honey is used for the treatment and prevention of numerous diseases. The medicinal properties and nutritional qualities of honey have been documented in Islamic, Christian, Vedic, Greek, Roman and other texts. Many scientists demonstrated that honey serves as a natural source of antioxidants, which are effective in reducing the risk of cancer, heart disease, different inflammatory processes, wound healing etc (Viuda-Martos *et al.*, 2008; Khan *et al.*, 2014)

The main antioxidants in this apiary product are phenolics and flavonoids. (Socha *et al.,* 2009; Bertoncelj *et al.,* 2007) Flavor and fragrance qualities of honey are very much dependent on the volatile and semi-volatile organic compounds present in both the sample matrix and aroma bearing compounds (Jerkoviae *et al.,* 2010). Unifloral honey has highly characteristic aromas, indicating the presence of Volatile Oil Compounds (VOCs) derived from nectar (Guyot *et al.,* 1999). Volatile substances are the main factors responsible for aroma, which along with other factors such as taste and physical factors contribute to the flavor (Baroni *et al.,* 2006)

Conversely, an elucidation of the origin of aroma compounds should lead to a better understanding of factors causing flavor differences between honeys. In addition, to characterize the aroma of honeys from different geographical areas of origin, considerations should be made based on the variability of weather conditions, proximity of the sea and beekeeping practices (Castro-Várquez *et al.,* 2010)

The present study was conducted for identification of Volatile Chemical Compounds in coriander floral honey processed by *Apis melifera*. This study will be useful for characterization of the floral honey from coriander .

Materials and methods

Sample collection

The unifloral honey samples of Coriander (*Coriandrum Sativum* L) from *Apis melifera* was collected from All India Coordinated Research Project on Honeybee and Pollinator, Voluntary Centre of Agricultural Research Station Kota, Rajasthan, India.

Sample processing

Honey sample was liquefied by heating the entire container containing raw honey in a hot water bath (70°C), followed by cooling to room temperature. Further the liquified honey was centrifuged to separate the honey from the bee wax. After centrifugation, the bee wax at the top of the liquid honey was separated, and the remaining liquid honey was filtered through a straining cloth. (Bruce, R.D. 2005). Five grams of honey solution was extracted successively with

*Corresponding author email: ishan.ullahkhan@gmail.com

methanol in soxhlet extractor for 8 hours. Brown coloured residues were obtained after concentrating the extract under reduced pressure using rotary evaporator. The obtained extracts were stored in desiccators for further analysis. The dried sample was re-dissolved in methanol to obtain 10 μg/mL concentrations. Finally, 2 ml of supernatant was taken and filtered through Axiva 0.2 μm nylon syringe filter and transfer to GC vial for analysis of the VOCs..

GC-MS conditions

GC-MS analysis was carried out on a Shimadzu GCMS-QP2010 Ultra system. The injector temperature was 280°C. The samples were injected in the split mode with split ratio 1/60. Injection volume was 1 μL. A capillary column Rtx-5MS (5% Diphenyl-95% Dimethyl Polysiloxane), 30 m × 0.25 mm × 0.25ìm, was used. Career gas was helium and constant flow of 1.00 mL/min was maitained.

The oven temperature was as follows: Initial temperature of 60°C, held for 2 min, increased to 10°C/min up to 260°C and held for 10 min. The MS ionization potential was 70 eV, and the temperatures were as follows: interface 260°C, Ion source 280°C. Mass scan range 40-550.

Results and discussion

GC-MS scan chromatograms (fig-1) of the methanolic extract of coriander floral honey showed number of biochemical constituents (Table 1). 27 compounds were identified and classified respectively in different chemical classes (Sugar, organic acids, alcohols, aldehyde and phenols). The identification of the chemical compounds was confirmed based on the peak area, retention time and molecular formula from National Institute for Standards and Technology (NIST) mass spectral library, ver. NIST 11 of Shimadzu GCMS-QP2010 Ultra.

The GC-MS profiling of coriander honey showed the presence several bioactive compounds which were mostly naturally accruing organic acid, flavour and fragrance compounds. The terpenes and other phyto-chemical constituents which were present in coriander essential oil and seed were not seen in coriander floral honey.

Sugar monosaccharide L-Glyceraldehyde (26.46%) wasfound in major quantity while other bioactive compounds were detected in trace amounts viz. 2-Oxoglutaric acid (0.36%), Acetyl isobutyryl (1.18%), Levulinic acid (1.15%), Acrylic acid (0.61%), Isobutyl formate (0.21%), Hydroxy dihydro maltol (1.72%), 2-Oxiranyl methanol (1.14%), Maltol (1.10%), Cyclohexyl ethyl ether (3.22%) 5-Hydroxy methyl furfural (1.96%), Glycerol alpha-monoacetate (7.40%), Propyl acetate (0.85%), 2,3-Dihydroxy propanal (14.02%), Mono methyl succinate (2.15%), 2-Hydroxy-2-methyl succinic acid (5.02%), n-Propyl acrylate (2.09%), Methyl 2-methoxy propanoate (3.21%), Nitro isobutyl glycerol (8.04%), Galacto-heptulose (4.88%), 3-Deoxy-d-mannoic lactone (6.74%), Eicosene (0.42%), Hexanedioic acid (0.95%), Phthalic acid, isobutyl octyl ester (1.11%), Benzene propanoic acid (0.24%), 1-Hepta triac otanol (0.62%) and Dodecenyl succinic anhydride (1.72%).

Maltol is a naturally occurring organic compound that is used primarily as a flavor enhancer. It is found in the bark of larch tree and in pine needles.Roasted maltol is used to impart a sweet aroma to fragrances. Eicosene generally found in wax material may have been detected due to the honeycomb. Hydroxy methyl furfural (HMF) is an organic compound derived from dehydration of certain sugars.Fresh honey contains less than 15 mg/kg HMF depending on pH-value and temperature (Rosatella *et al.,* 2011 Ruiz-Matute *et al.,* 2010).

Honey is a very complex product, because its properties and composition depend not only on the nectar-providing plant species, but also on other factors such as bee species, geographic area, season, mode of storage, and even harvest technology and conditions (Kaskoniene *et al.,* 2010). However, honeys produced from different floral sources may have distinctly different aromas and tastes due to differences in volatile composition, which in turn is dependent on the extraction methods and also on the botanical and geographical origins (Jerkovic *et al.,* 2010). Bentivenga *et al.,* (2010) reported the presence of aromatic hydrocarbons which represents an indication of environmental problem in honey obtained from *Basilicata* which were used to monitor environmental pollution caused by oil extraction.

Nurul Syazan (2013) identified 35 volatile compounds in which hydrocarbons constituted 58.5% of the composition of Tualang honey. Other classes of chemical compounds detected included acids, aldehydes, alcohols, ketones, terpenes, furans and some miscellaneous group. Methanol yielded the highest number of extracted compounds such as acids and 5-(Hydroxy methyl furfural (HMF).

Castro-Várquez *et al.,* (2010) differentiated chestnut honeys from north-east, north-west and south- east areas of Spain based on the significant differences in concentration of several volatile compounds and sensory characteristics pertaining to aroma.

Wolski *et al.,* (2006) Investigated 4 different floral honeys that were multifloral, heather, buckwheat and lime-honeydew and found 86 compounds from different chemical classes, for instance: alcohols, phenols, ketones, organic acids, esters and hydrocarbons (aliphatic, aromatic and cyclic). The performed analysis showed that the obtained volatile profiles of the examined honeys differed and they concluded that analysis of the volatiles

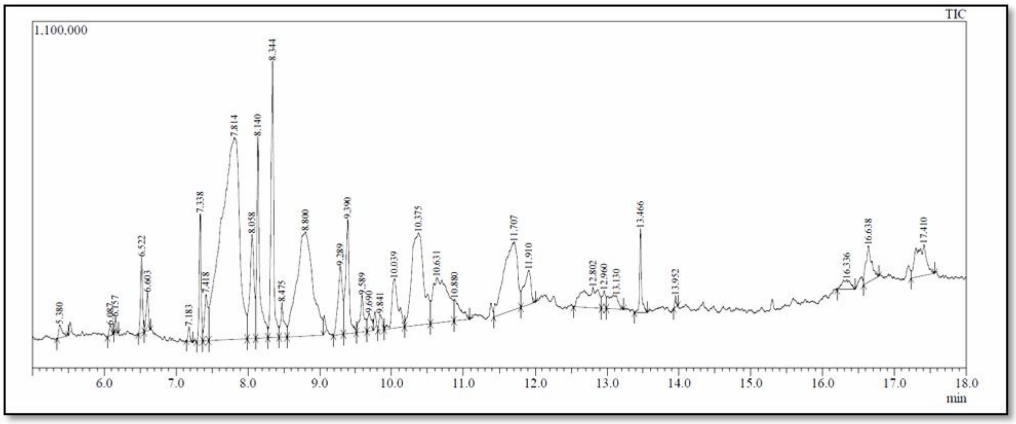

Fig. 1: GC-MS chromatogram of coriander floral honey

Table 1. Volatile Bio-chemicals compounds of coriander floral honey identified by GC-MS

Peak	Compound Name	R. T.	Area %	Molecular Weight	Molecular Formula	CAS No.
1.	2-Oxoglutaric acid	5.380	0.36	146	$C_6H_8O_4$	328-50-7
2.	Acetyl isobutyryl	6.087	1.18	114	$C_6H_{10}O_2$	7493-58-5
3.	Levulinic acid	6.157	1.15	116	$C_5H_8O_3$	123-76-2
4.	Maltol	6.522	1.10	126	$C_6H_6O_3$	118-71-8
5.	Acrylic Acid	6.603	0.61	128	$C_6H_8O_3$	106-90-1
6.	Isobutyl formate	7.183	0.21	102	$C_4H_{10}N_2O$	30533-08-5
7.	Hydroxy dihydro maltol	7.338	1.72	144	$C_6H_8O_4$	28564-83-2
8.	2-Oxiranyl methanol	7.418	1.14	74	$C_3H_6O_2$	60456-23-7
9.	L-Glyceraldehyde	7.814	26.46	90	$C_3H_6O_3$	497-09-6
10.	Cyclohexyl ethyl ether	8.058	3.22	128	$C_8H_{16}O$	932-92-3
11.	5-Hydroxymethylfurfural	8.140	1.96	126	$C_6H_6O_3$	67-47-0
12.	Glycerol alpha-monoacetate	8.344	7.40	134	$C_5H_{10}O_4$	106-61-6
13.	Propyl acetate	8.475	0.85	102	$C_5H_{10}O_2$	109-60-4
14.	2,3-Dihydroxy propanal	8.800	14.02	90	$C_3H_6O_3$	497-09-6
15.	Monomethyl succinate	9.289	2.15	132	$C_5H_8O_4$	3878-55-5
16.	2-Hydroxy-2-methyl succinic acid	9.390	5.02	148	$C_5H_8O_5$	6236-09-5
17.	n-Propyl acrylate	9.589	2.09	114	$C_6H_{10}O_2$	925-60-0
18.	Methyl 2-methoxypropenoate	10.039	3.21	116	$C_5H_8O_3$	7001-18-5
19.	Nitroiso buty lglycerol	10.375	8.04	151	$C_4H_9NO_5$	126-11-4
20.	Galacto-heptulose	10.631	4.88	210	$C_7H_{14}O_7$	0-00-0
21.	3-Deoxy-d-mannoic lactone	11.707	6.74	162	$C_6H_{10}O_5$	0-00-0
22.	Eicosene	12.960	0.42	280	$C_{20}H_{40}$	74685-30-6
23.	Hexanedioic acid	13.130	0.95	146	$C_6H_{10}O_4$	124-04-9
24.	Phthalic acid, isobutyl octyl ester	13.466	1.11	334	$C_{20}H_{30}O_4$	0-00-0
25.	Benzene propanoic acid	13.952	0.24	292	$C_{18}H_{28}O_3$	6386-38-5
26.	1-Heptatriaocotanol	16.336	0.62	536	$C_{37}H_{76}O$	105794-58-9
27.	Dodecenyl succinic anhydride	27.989	1.70	266	$C_{16}H_{26}O_3$	19780-11-1

RT : Retention time

could be effective for the characterization of the botanical source of honeys.

Conclusion

The above mentioned research findings show the presence of bioactive components in honey and the wide dissemination of this knowledge, has led to a general acceptance that honey is a respectable therapeutic agent with rapidly increasing uptake by clinicians as well as by the general public. The finding that there are multiple bioactive components involved in the therapeutic action makes it a much more attractive option to be used as natural product. On other hand volatile profiles of the coriander honeys differed from other floral honey which could be effective for the characterization of the coriander floral honeys.

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