Classification of Yucatan Peninsula honeys by aroma volatile compounds

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INTRODUCTION

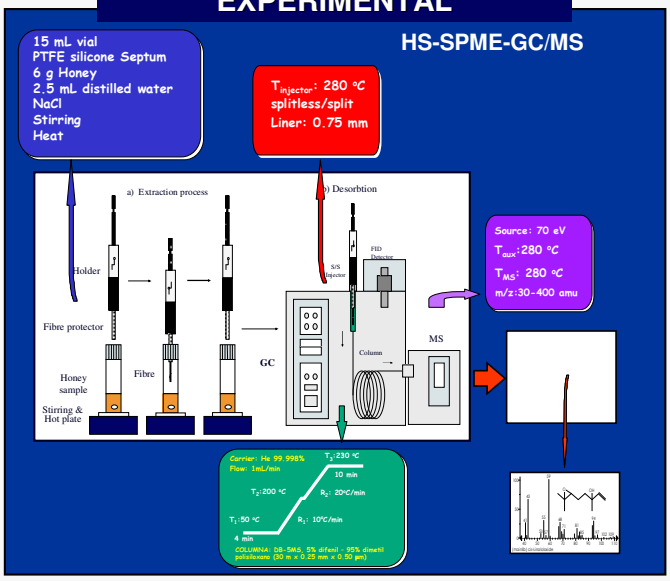
Honey is greatly appreciated by consumers, not only for its nutritive and medicinal properties, but also for its characteristic aroma and sweet taste. Aroma is a result of the presence in honey of many volatile compounds.[1] Some of them come from the nectar or honeydew collected by bees and others originate during the honey processing or storage.[2-4]

Consumer choice is linked to organoleptic characteristics and these depend on the botanical origin of the product. In order to determine the botanical origin of honey, the analyst must do a sensory test, physicochemical analysis, and pollen analysis. [5] The characterization of botanical or floral origin of honey by GC or GC/MS analysis of volatile compounds has been reviewed recently. [6] Several approaches have been made for this purpose. Of all extraction techniques HS-SPME is the best approach as a solvent-free and inexpensive, together with its reliable detection of low concentrations of analytes.

The Yucatan peninsula is the most important region of honey production in Mexico; 30% of the total amount of Mexican honey for export is obtained from this area. The sources of the most widely produced unifloral honeys in the Yucatan peninsula are: *Tahonal* (*Viguiera dentata* Blake, var. *heliantoides*), *Tzitzilché* (*Gymnopodium floribundum* Rolfen) and *Haabín* (*Piscidia piscipula* L.).

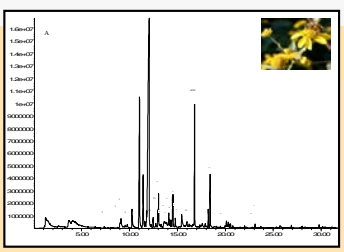
The aim of this investigation was to differentiate certain unifloral Mexican honeys by means of a simple procedure based on PCA statistical analysis of the honey's volatile compounds, analysed by HS-SPME-GC/MS.

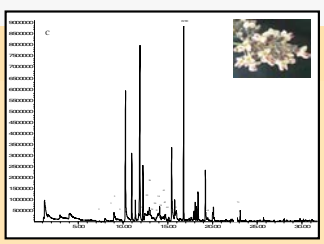
EXPERIMENTAL



Identification of volatile compounds was made by comparing their mass spectra with two libraries (NIST 02, and our specific library for volatile compounds, FLAVORLIB).

Quantisation was carried out by comparing the peak area of each compound with that of the internal standard (Fig. 1).





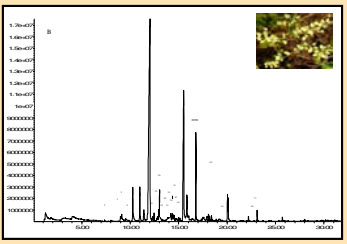


Figure 1. TIC chromatograms of unifloral honeys: A) *Tahonal*, B) *Tzitzilché*, C) *Haabín*.

RESULTS

Throughout the aroma profiles, the honeys were classified by using PCA.[7] The number of volatile compounds was reduced to 21, as these compounds presented a major variability between samples analysed. The selected compounds were those that corresponded to chromatographic peaks 2, 3, 5, 9, 18, 22, 26, 28, 30, 31, 34, 38, 41, 42, 44, 49, 51, 62, 64, 69, and 71 (Table 1). By using multivariable statistical analysis it was possible to obtain the distribution of many variables of a system, which in turn is useful to perform the synthesis of the internal iterations of the entire system. In this work we were able to compare statistically throughout a group of typical aroma components, honeys of different unifloral origins.

Factor loadings for each compound provide an indication of the importance of the original variable over the principal component (Table 1). Thus, benzaldehyde, *p*-cymene, *trans*-linalool oxide, ethyl octanoate, ethyl anisate and 1,3-diisipropylbenzene are the compounds that contribute more significantly to principal component PC1. For PC2, the epi-α-cadinol, 2,3-dimethoxytoluene and unidentified compound 2 are the compounds that more significantly contribute, and for PC3 only *p*-mentha-1,5-dien-8-ol contribute more significantly.

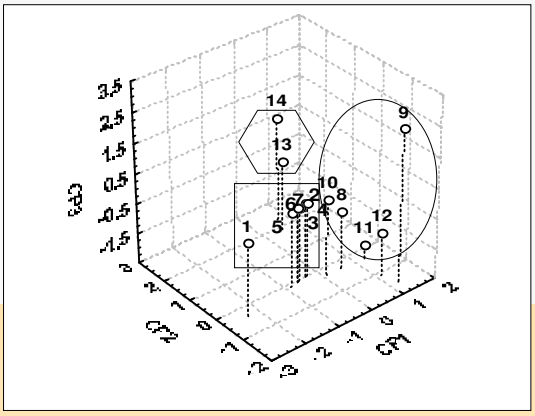


Figure 2. 3D graph of principal component analysis. Grouped by using geometrical forms, differences are observed between honeys of *Tahonal* (square), *Tsitsilché* (oval) y *Haabín* (hexagon).

PCA results for the 14 honey samples are given in Fig. 2, where three groups comprised of *Tzitzilché* honey (samples 8 to 12, differentiated by the first principal component PC1>0 and the second component PC2<0), *Tahonal* honey (samples 1 to 7, differentiated by PC1<0 and PC=0) and *Haabín* honey (samples 13 and 14, differentiated by PC1>0 and PC2≥2) are observed. The contribution of the third principal component is irrelevant for classification of the samples.

Principal components PC1 and PC2 produced 53.4% of variance explanation, while PC3 produced 14.3%; both generated 67.9% of the total variance explanation which is high, given the heterogeneity of the chemical composition of the samples (Table 2).

Table 1. Variable loading factors of volatile compounds in honeys from the Yucatan peninsula, Mexico

Peak	Compound	KI	CP1	CP2	CP3
2	Benzaldehyde	960	0.7899*	0.0750	0.0617
3	6-Methyl-5-hepten-2-one	986	0.3658	-0.0967	-0.5716
5	Octanal	999	0.4979	0.3613	-0.4871
9	*p*-Cymene	1026	-0.8071*	-0.0594	-0.0145
18	Methyl octanoate	1105	0.2135	0.6675	0.2966
22	Phenylacetonitrile	1144	0.4258	-0.4444	-0.1229
26	*p*-Vinylanisole	1153	0.6626	-0.5202	0.2127
28	*p*-Mentha-1,5-dien-8-ol	1166	0.4029	-0.4844	0.7000*
30	*trans*-Linalool oxide (pyranoid)	1178	-0.8139*	-0.1188	-0.0116
31	Methyl 2-phenylacetate	1176	0.4308	-0.5249	0.6607
34	Ethyl octanoate	1197	-0.7750*	-0.1122	-0.010
38	Unidentified 1	1216	0.4771	-0.4581	0.5978
41	Unidentified 2	1238	0.2710	0.8874*	0.1834
42	Benzyl ethyl ketone	1239	0.5619	-0.4282	-0.4682
44	2,3-Dimethoxytoluene	1242	0.2562	0.8463*	0.1289
49	α-Methylcinnamaldehyde	1268	0.2104	0.6631	0.2979
51	Phenylacetic acid	1270	0.5230	-0.3568	-0.6160
62	Dodecanal	1409	0.4586	0.0939	-0.5015
64	Ethyl anisate	1444	-0.8906*	-0.1182	-0.0056
69	*epi*-α-Cadinol	1632	0.2467	0.8181*	0.1048
71	1,3-Diisopropylbenzene	1645	-0.7058*	-0.1075	-0.0127

Table 2. Results of the principal component analysis

PC	Eigenvalue	Total variance (%)	Accumulated variance (%)
1	6.4974	30.94	30.94
2	4.7675	22.70	53.64
3	3.0009	14.29	67.93

CONCLUSION

By using HS-SPME-GC/MS combined with principal component analysis it is possible to differentiate between these three types of Yucatan peninsula unifloral honeys by means of the evaluation of 21 volatile compounds present in their aroma profiles.

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