REPORT

CHEMICAL COMPOSITION OF EGYPTIAN AND UAE PROPOLIS

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ABSTRACT

The chemical composition of propolis samples obtained from Behera, Egypt and Dubai, UAE, have been investigated by GC-MS and thirty four compounds have been tentatively identified. Some of these compounds have not been reported previously in Egyptian propolis from different regions. The Egyptian sample contains a high amount of aliphatic (13.7%) and aromatic (14.4%) acids. The alcohols, phenols and esters account for about 17.0% of the total content analysed. Some anthraquinone and flavone derivatives have also been detected (10%). The UAE sample is characterised by the presence of a high content of aliphatic acids (15.2%) and a low content of aromatic acids (4.3%). The aldehydes, alcohols, phenols and esters amount to about 9%. In addition to these some other compounds (high molecular weight alkanes, sugar derivatives, anthraquinone derivatives and flavone derivatives) are also present to the extent of about 33%.

Keywords: Egyptian propolis, UAE propolis, chemical composition, GC-MS analysis.

INTRODUCTION

Propalis (bee glue) is a dark-coloured resinous substance collected by bees from poplar buds and other plants and used to seal their hives. It has traditionally been used for a variety of disorders and for its antibacterial properties (Bankova *et al.*, 2000; Burdock 1998; Gallo and Savi 1995; Grange and Davery 1990; Koo *et al.*, 2002; Krol 1993; Nagaoku *et al.*, 2003; O'Neal 2001; Orsolic and Basic 2003; Oztruk *et al.*, 1999; Parfitt 1999; Park *et al.*, 1998; Sa-Nunes *et al.*,2003; Vanhaelen 1979; Volpert and Elstner 1996) and its extracts and other preparations are available in the market. Several workers have investigated the chemical composition and antimicrobial properties of propolis of different origin including the Egyptian (Hegazi and Abd El Hady 2001; 2002 Abd El Hady and Hegazi 2002), Turkish (Keskin *et al.*, 2001; Sorkun *et al.*, 2001; Popova *et al.*, 2005), Tunisian (Martos *et al.*, 1997), Moroccan (Rhajaoui *et al.*, 2001), Greek (Melliou and Chinou 2004), Brazilian and Bulgarian (Bankova *et al.*, 1995; Pereira *et al.*, 2000; Velikova *et al.*, 2000; Salomao *et al.*, 2004), Hungarian (Papay *et al.*, 1986), British (Greenway *et al.*, 1988), Mediterranean (Velikova *et al.*, 2000) and European propolis (Bankova *et al.*, 2000; Hegazi *et al.*, 2000). Attempts have been made to standardize propolis (Bankova and Marekov 1984; Volpert and Elstner 1993; Arvouet-Grand 1994; Miyataka *et al.*, 1997; Marcucci *et al.*, 2000) and to determine the quality of its samples from various sources (Bankova 2000; Serra Bonvchi and Venhira Coll 2000).

The present study is based on an investigation of the chemical composition of propolis samples of Egyptian (Behera) and UAE (Dubai) origin using gas chromatography-mass spectrometry (GC-MS). This is the first study of the chemical composition of UAE propolis.

MATERIALS AND METHODS

Propolis samples

Samples of propolis were obtained from reclaimed land at Behera near Alexandria, Egypt, and from Dubai, UAE, and were stored for one week at 4°C before use.

Equipments

The GC-MS system consisted of a Hewlett-Packard (HP) series 6980 gas chromatograph interfaced with a model 5973 HP mass selective detector (Palo Alto, CA, USA) using a HP 5MS column (cross-linked 5% methylphenyl silicone, 30 m × 0.25 mm i.d., 0.25 µm film thickness).

Methods

I Extraction and sample preparation

The samples of propolis were extracted with 70% ethanol according to the method of Hegazi and Abd El Hady (2002) and the balsam subjected to GC-MS analysis either directly or after derivatisation with TMS.

II GC-MS analysis

The GC-MS analysis was performed by temperature programming. The column oven temperature was initially held at 100°C for 2 min, then programmed to rise to 280°C at a rate of 20°C/min and held for 5 min. The total run-time was 16 min. The temperatures of the injector port and the interface were set at 250 and 280°C, respectively. The carrier gas (helium) flow rate was 1.0 ml/min. The ionization energy was set at 70 eV. The mass spectra were collected by scanning from m/z 50 to m/z 550 at two second intervals.

III Identification of compounds

The identification of various compounds present in propolis

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Table 1: Chemical composition of ethanolic extracts of Egyptian (Behere) and UAE (Dubai) Propolis

Compounds	Behera propolis	Dubai propolis
	% TIC**	
Aliphatic acids		
Malic acid	1.92	1.18
*Succinic acid	-	1.11
Palmitic acid	3.12	2.99
Oleic acid	3.18	3.12
Octadecenoic acid	3.29	2.87
*Octadecadienoic acid	0.59	-
Stearic acid	1.57	1.78
*Tetracosanaoic acid	-	2.18
Aromatic acids		
*2-Amino-3-methoxybenzoic acid	3.18	-
*Benzenepropionic acid	0.90	-
Cinnamic acid	2.04	-
*4-Hydroxycinnamic acid	2.85	-
*4-Methoxycinnamic acid	2.80	-
Caffeic acid	2.59	2.35
* Ferulic acid	-	1.95
Alcohols/ Phenols/ Aldehydes		
Glycerol	2.76	2.32
*2-Naphthalenemethanol derivatives	4.78	2.71
*2-Methoxy-4-vinylphenol	4.10	-
*Butyraldehyde	-	2.48
Esters		
*4-Methoxyhydrocinnamate	2.77	-
*3-Methyl-3-butenyl isoferulate	2.55	-
*Ethyl palmitate	-	3.88
Others		
*d-Xylose	-	2.95
*Glucofuranose derivative	-	2.86
*5,7-Dihydroxyflavone	0.30	-
*5,7-Dihydroxydihydroflavone	2.75	-
*1,7-Dihydroxy-3-methoxy-6-methylanthraquinone	0.67	-
*1,3,8-Trihydroxy-6-methylanthraquinone	-	1.10
*1-(Dihydroxyphenyl)-3-phenylpropenone	4.50	-
*5-Hydroxy-7-methoxy-2-phenyl- 4H-1-benzopyran-4-one	2.78	-
*Tricosane	-	11.90
*Octacosane	-	8.49
*Docosane	-	4.24
*Pentatricosane	-	0.99

*Compounds not reported in Egyptian propolis (Hegazi abu El Hady 2002) and tentatively identified by GC-MS analysis.
**TIC = The ion current generated by a compound depends upon its characteristics and is not a true measure of quantitation.

samples was carried out by computer search on MS database libraries on the basis of mass spectral fragmentation. The available reference compounds were co-chromatographed to confirm GC retention times. Some compounds could not be identified due to the lack of authentic samples and their library spectra.

RESULTS AND DISCUSSION

I Chemical composition of Egyptian and UAE propolis

The chemical composition of the ethanolic extracts of Behera propolis has been determined by GC-MS analysis. A total of thirty four compounds have been tentatively identified in this study. Some of the compounds detected in Behera samples have not been previously reported in the Egyptian propolis (Hegazi and Abd El Hady 2000). The details of various compounds including aliphatic acids, aromatic acids, alcohols, phenols, esters and other compounds found in the Egyptian and UAE samples are given in table 1. The major compounds found in the Egyptian propolis are aliphatic acids (13.7%), aromatic acids (14.4%) and alcohols, phenols and esters (17.0%). The presence of a significantly high amount of flavone and benzopyranone derivatives (5.8%) compared to the flavonoids reported by Hegazi and Abd El Hady (2000) in Egyptian propolis has been noted. Some other compounds including an anthraquinone derivative is also present in small amount (0.67%).

The GC-MS analysis of UAE propolis showed the presence of twenty compounds (table 1). These include a high content of aliphatic acids (15.2%) and a low content of aromatic acids (4.3%). The aldehydes, alcohols, phenols and esters account for 11.4%. Other compounds, including high molecular weight alkanes, sugar derivatives, anthraquinone derivatives and flavone derivatives, are present to the extent of 32.5%. Some of the simple compounds detected (e.g. glycerol, d-xylose) may result from the degradation of complex constituents in propolis.

Variations in the chemical nature of propolis of different origin have been observed by many workers (Papay *et al.*, 1986; Greenway *et al.*, 1988; Abd El Hady and Hegazi 2002; Bankova *et al.*, 1995, 2000; Martos *et al.*, 1997; Pereira *et al.*, 2000; Hegazi *et al.*, 2000; Velikova *et al.*, 2000, 2002; Hegazi and Abd El Hady 2001, 2002; Keskin *et al.*, 2001; Rhajaoui *et al.*, 2001; Sorkun *et al.*, 2001; Melliou and Chinon 2004; Salomao *et al.*, 2004; Popova *et al.*, 2005). It may be pointed out that even the two Egyptian samples of propolis (El-Saff and Ismailia) have been found to possess different chemical composition (Hegazi and Abd El Hady 2002). It is worth noting that the majority of the compounds detected in the samples of Behera propolis are different from those present in the Egyptian propolis of other origin that has previously been investigated (Hegazi and Abd El Hady 2002). This may be due to some difference in the source of poplar buds and other plants from which the propolis is collected. The chemical variations in Dubai propolis compared to those of the other Egyptian regions may impart it some specific therapeutic activity. However, further investigation is needed to evaluate the biological activity of the Dubai propolis.

II Stability of propolis

An important factor to be considered in the study of propolis samples of different origin is their sensitivity to environmental stimuli, e.g. moisture, heat, light, etc., affecting the stability of propolis and causing chemical changes so as to alter the true composition of the material. The samples collected from different regions should immediately be subjected to proper storage conditions to avoid degradation of active constituents. Strict temperature, light and moisture control during storage is necessary to keep the sensitive constituents intact (Handa Data Sheet, Oxis Research). Esters and amides are sensitive to moisture and temperature and may degrade under improper storage conditions. The thermal stabilities of ethanolic extracts of propolis collected in Taiwan have been studied (Lu *et al.*, 2003). High temperature high resolution GC-MS may lead to the degradation of some heat sensitive components of propolis (Pereira *et al.*, 1999). The aromatic and heterocyclic compounds and flavones and anthraquinones are sensitive to light and may undergo oxidative degradation (Tonnesen, 1996). The chemical changes in propolis of any origin due to environmental factors may alter the therapeutic activity of the material and thus make it relatively less useful.

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