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Macroelements in dietetic products containing propolis

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Abstract

This work quantifies sodium, potassium, calcium, and magnesium in propolis dietetic products. These macroelements have been determined in four different formulations: tablets, capsules, ampoules and syrups using Atomic Absorption Spectroscopy. © 1999 Elsevier Science Ltd. All rights reserved.

1. Introduction

The functions performed by the human body are the result of the different processes of various systems and organs. These processes, in turn, involve different cellular metabolic pathways which require nutrients ingested via the diet.

Micronutrients constitute a small proportion of food but are, nevertheless, essential for the normal functioning of the body and take part in many of the reactions occurring in the human organism. Deficiencies in this type of nutrient may be alleviated by the wide range of new products on the market known as 'dietary products' (Mills, 1986).

Many of the dietary preparations currently available contain propolis as the major component. Propolis is a resinous substance collected by bees as an exudate from the bark of various plants. It is composed of resin, several phenolic compounds (mainly flavonoids) and a series of essential oils. The presence of pollen adds to its nutritional value and, in dietary supplements, propolis is often accompanied by other products such as various types of plants, honey, royal jelly and pollen (Root, 1984; Philippe, 1990; Bonet, 1994).

The aim of the present investigation was to determine the levels of the macroelements; sodium, potassium, calcium and magnesium, of different pharmaceutical preparations containing propolis. These preparations are mainly sold in health food stores but are becoming more widely accepted by consumers as a supply of minerals and a complement to the general diet.

2. Materials and methods

2.1. Sample description

The levels of Na, K, Ca and Mg in 15 commercial brands of propolis were determined. The products were purchased from health and dietary stores of Madrid.

The different preparations of commercially available products based on propolis led to the classification of samples into two main groups: solid preparations (tablets and capsules) and liquid preparations (ampoules and syrups). Four samples of each type of preparation were analyzed with the exception of the ampoules (only three brands are available on the market due to their reduced popularity among the consumers).

The samples were categorized according to the following identification codes:

(a) Tablets: TA.1 to TA.4
(b) Capsules: CA.1 to CA.4
(c) Ampoules: AM.1 to AM.3
(d) Syrups: SY.1 to SY.4

2.2. Preparation of samples

2.2.1. Solid preparations

The tablets and contents of capsules were ground in a mortar to obtain a 1.5 g sample of the homogenized product.

2.2.2. Liquid preparations

Liquid forms were thoroughly mixed prior to analysis.

2.3. Analytical methods

Once weighed, the samples were carbonized by incineration. The calcination temperature did not surpass

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450°C. Liquid forms were previously heated in a water bath to obtain extracts.

The ashes were collected in 50% acid medium (HCl/HNO_3) and made up to a volume of 50 ml (Torija, 1981). The Na, K, Ca and Mg levels of these solutions were determined by atomic absorption spectroscopy using a Perkin Elmer 2280 spectrophotometer (acetylene air flame and hollow-cathode lamps). Calibration curves were prepared for standard solutions and used to calculate the concentration of the solution required for estimation of each element. Results are expressed as mg $100\,g^{-1}$ of product.

Due to their high concentrations, Na and K levels were estimated in diluted samples. Prior to the determination of Ca and Mg, samples were diluted in lanthanum oxide.

3. Results and discussion

The results obtained may be summarized as follows:

Fig. 1 shows the contents according to the manufacturer listed on the product container. Tables 1 and 2 quote the levels of sodium, potassium, calcium and magnesium in the solid and liquid preparations. Tables 3 and 4 show statistical data related to the levels of each macroelement.

Large quantities of macroelements were found in all the samples. Significantly greater amounts were found in the solid preparations than in liquid forms (especially ampoules).

Sodium was found in abundance in all the samples. Lowest sodium levels were found in the ampoules, ranging from 4.80 mg % for AM.3 and 18.2 mg % for AM.1 (Table 2). These values were considerably lower than those obtained for the syrups which showed a minimum sodium content of 25.8 mg % for SY.2 and maximum of 183 mg % for SY.3. Sample SY.4 was shown to contain 52.3 mg % Na, a value considerably lower than the Na content of SY.3. Fig. 1 shows that SY.4 is enriched with several components including 500 mg propolis extract, suggesting that the reduction in sodium and general mineral content with respect to syrup sample 3 is due to a large quantity of propolis in SY.3 which is not specified on the label.

The sodium levels of the tablets (Table 1) showed greater variability than those of the capsules. Maximum sodium levels were found in sample TA.4 (136 mg %). This product contains haw, a fleshy bitter-sweet fruit which is widely used in the preparation of fruit preserves and jellies and is also enriched with oligoelements and yeast (Fig. 1). Minimum Na levels were found in sample TA.3 (19.5 mg %). This product is enriched with plant extracts (*Echinacea angustifolia*, sage) which, due to

SOLID PREPERATIONS		LIQUID PREPERATIONS	
TABLETS		**AMPOULES**	
TA.1	Dextrose, propolis, honey, malt, antiagglomerant (magnesium stearate) and aroma.	**AM.1**	Royal jelly (300 mg), propolis extract (100 mg), vitamin E (10 mg) and deionized water
TA.2	Saccharose, lactose, papaya, propolis and vitamin C.	**AM.2**	Honey, stabilizing agent (glycerol) and propolis (500 mg)
TA.3	Propolis (50 mg), *Echinacea angustifolia* extract (25 mg), vitamin C (50 mg) and sage extract.	**AM.3**	Concentrated natural extract of propolis.
TA.4	Haw (110 mg), dry propolis extract (50 mg),, *Echinacea* (110 mg), dry willow extract (150 mg), yeast rich in copper (60 mg) and in cobalt (20 mg).		
CAPSULES		**SYRUPS**	
CA.1	Contents not specified	**SY.1**	Eucalyptus honey, cane molasses, propolis extract, yeast, polen, mint and eucalyptus essence.
CA.2	Propolis (300 mg) and *Echinacea angustifolia* (300 mg).	**SY.2**	Honey, propolis extract, mallow infusions, thyme, willow and pine essence.
CA.3	Propolis (250 mg), gelatine, talc, silicon dioxide, corn starch and magnesium stearate.	**SY.3**	*Echinacea angustifolia*, propolis, *Thymus vulgaris*, and vegetable glycerine
CA.4	Contents not specified	**SY.4**	Apple juice, honey, plant infusion 2.7 % extract (*Echinacea*, *"sol de oro"*, *Chlorella alga*, birch, hazlenut leaves, juniper, sarsaparilla, garlic and angelica), propolis extract (500 mg), iron and copper gluconate, aroma.

Fig. 1. Composition according to label.

Table 1
Macroelements in commercially available propolis preparations: tablets and capsules

Samples	Na	K	Ca	Mg
Tablets				
TA.1	113	30.0	41.5	194
TA.2	43.0	38.6	23.7	104
TA.3	19.5	15.2	86.7	5.50
TA.4	136	285	834	83.9
Capsules				
CA.1	47.7	19.0	67.5	8.72
CA.2	250	280	251	142
CA.3	83.0	31.5	301	70.4
CA.4	50.8	25.4	90.2	10.3

Results expressed as mg $100\,g^{-1}$ product.

Table 2
Macroelments in commercially available propolis preparations: ampoules and syrups

Samples	Na	K	Ca	Mg
Ampoules				
AM.1	18.2	6.26	9.17	3.00
AM.2	9.76	17.8	7.50	2.53
AM.3	4.80	8.86	7.60	2.50
Syrups				
SY.1	39.3	152	24.7	15.0
SY.2	25.8	59.6	32.4	11.0
SY.3	183	217	44.9	68.3
SY.4	52.3	205	29.5	14.0

Results expressed as mg $100\,g^{-1}$ product.

their essential oils, contribute to the balsamic effect of propolis but do not affect sodium levels.

Capsules generally showed less variable Na values. These ranged from 47.7 mg % for CA.1 and 250 mg % for CA.2. The latter value was the maximum obtained in all the samples. The ingredients of this product include similar proportions of *Echinacea angustifolia* and propolis (300 mg per capsule), suggesting that Na is provided mainly by the plant extract given that it contains similar amounts of propolis to CA.3. This latter sample contains 250 mg propolis in addition to other compounds which are unlikely to contribute to the Na level but, nevertheless, contains a third of the Na concentration of CA.2 (83.0 mg %) (Fig. 1, Table 1).

The determination of potassium levels revealed that although fairly variable, these fell within ranges which were narrower than those obtained for sodium with the exception of the syrups. This type of preparation showed the widest range of K levels with a maximum value of 217 mg % for SY.3 and a minimum of 59.6 mg % for SY.2. In contrast, ampoules showed K levels above 6 mg %. Sample AM.2 containing 17.8 mg % K is enriched with honey and 500 mg propolis. These ingredients probably contribute to the K level (Souci, 1994).

The similarity in K levels of AM.1 and AM.3 merits some attention (Table 2). The former product contains 300 mg royal jelly which might be expected to increase the level of this cation. This sample contains a small amount of propolis extract (100 mg per ampoule) whereas the manufacturers of the latter sample include 'natural concentrated extract' in the contents, which suggests the presence of a larger amount of propolis explaining the slight increase in K.

Sample TA.4 is described by the manufacturer to contain 'yeast rich in copper and cobalt'. The latter has been reported to contain 649 mg % K (Souci et al., 1994) justifying its high concentration of this element in comparison to the other tablets. These show a minimum K value of 15.2 mg % (TA.3) and contain only small amounts of propolis (50 mg tablet). TA.3 is also enriched with plant extracts (*Echinacea angustifolia* and sage).

The sample richest in K was capsule CA.2 (280 mg %). This sample also contained the greatest amount of Na due to enrichment with *Echinacea angustifolia*. Minimum K values were seen in CA.1 and CA.4 (19.0 mg % and 25.4 mg %, respectively) (Table 1), samples manufactured by different companies. The manufacturers do not specify their contents and only provide formulations with respect to macronutrients. This composition is similar for the two brands and does not affect the levels of this cation.

Calcium was the major element found in the solid preparations although the calcium content of the ampoules and syrups resembled that of sodium.

Calcium levels of tablets ranged from 23.7 mg % for TA.2 to 834 mg % for TA.4 (Table 1). The latter sample is enriched with several components (Fig. 1) and, given that both samples contain similar amounts of propolis, these are thought to contribute to the Ca content of the sample. The formulation of sample TA.2 includes sugars, vitamin C, papaya (tropical fruit containing 20.7 mg % Ca) and propolis representing low Ca enrichment. However, the presence of lactose aids the absorption of this element.

The calcium levels recorded for the capsules may be divided into two groups: CA.1 and CA.4 contained 67.5 mg % and 90.2 mg % Ca, respectively, and CA.2 and CA.3 showed values of 251 mg % and 300 mg %, respectively (Table 1). These values are confirmed by the enrichment of the latter two products. The contents of samples with lower Ca levels are not specified (Fig. 1).

Finally, the liquid forms showed a low variability of Ca levels within each group. Sample AM.1 contained the highest amount of Ca of the ampoules, 9.17 mg % and SY.3 showed the maximum Ca content of the syrups (44.9 mg %)(Table 2).

Magnesium was also found in greater quantities in the solid preparations. Tablet sample TA.1 showed a

Table 3
Statistical analysis of levels of macroelements in the different types of preparation. (Kruskall Wallis Test)

Pharmaceutical preparation	Macroelements			
	Sodium (Mean range)	Potassium (Mean range)	Calcium (Mean range)	Magnesium (Mean range)
Tablets	36.0/4 = 9.00	34.0/4 = 8.50	38.8/4 = 9.70	44.0/4 = 11.0
Capsules	43.0/4 = 10.75	33.0/4 8.25	49.0/4 = 12.25	36.0/4 = 9.00
Ampoules	6.00/3 = 3.00	7.00/3 = 2.33	6.00/3 = 2.00	6.00/3 = 2.00
Syrups	35.0/4 = 8.75	46.0/4 = 11.5	27.0/4 = 6.75	34.0/4 = 8.50
p value	0.0651	0.0621	0.0206	0.0589

particularly high Mg content of 194 mg % due to the stearate antiagglomerant. In contrast, tablet sample TA.3 contained the smallest amount of this element, 5.50 mg %, due to enrichment with plant extracts and vitamin C and a smaller proportion of propolis (50 mg per tablet).

Table 1 shows that maximum Mg levels in the capsules occur in CA.2 (142 mg %), attributable to *Echinacea angustifolia*. Capsules CA.1 and CA.4 contain similar levels of Mg, 8.72 mg % and 10.3 mg %, respectively, as recorded for Na, K and Ca. CA.3 was shown to contain 70.4 mg % Mg. Given the presence of magnesium stearate and talc, this value seems low in comparison with that of sample CA.2.

The Mg content of the ampoules was similar in each sample and within the range 2.50 to 3.00 mg % (Table 2). This homogeneity was also seen in the syrup samples, although levels were of the order of 11 mg % with the exception of SY.3. This sample showed a Mg level of 68.3 mg % due once again to the presence of *Echinacea*.

3.1. Statistical analysis

Since there was a high degree of variability between the levels of minerals found in the four types of preparation and also within each preparation group, the statistical analysis performed did not take into account mean levels but considered each range of values. To this end, the statistics package BMDP3S was employed. First of all, a non-parametric ANOVA test (Kruskal Wallis model) is applied to the data. This test takes into account the total number of samples used (15) to detect differences between the different dietetic products analysed.

This statistical model first establishes the range comprising each variable (the commercial preparation of the product). The data obtained are ranked from high to low and a value is assigned to each variable (tablets, capsules, ampoules and syrups). This value is termed the rank sum and is used to calculate the mean range of values shown in Tables 3 and 4. Comparison of the four mean range values gives rise to a *p* value or level of significance which is also shown in the tables. The closer *p* is to zero the greater is the degree of confidence establishing differences between variables. Mean ranges and *p* values are summarized in Table 3.

The *p* values relating to the different macroelements in no case reached 0.00. The *p* value for calcium was the lowest and most significant ($p = 0.0206$) denoting the greatest variability between the four preparation groups. Sodium, potassium and magnesium showed a significance level of 0.06 confirming this variability of results to a lesser extent.

Once these differences were established, multiple comparison was performed to compare every possible combination of pairs of variables. This was used to establish similarity between pairs with respect to the range of mineral level, giving rise to *z* stat (Table 4). It may be observed that for a *z* stat between 2 and 2.64, *p* equals 0.10, or it may be stated with 90% confidence that there is no similarity between the two groups. When *z* stat > 2.64, *p* equals 0.05, i.e. there is a 95% chance that a difference between pairs exists.

Table 4 shows considerably high *z* stats for sodium, potassium, calcium and magnesium. The values of 3.00 for calcium, for the ampoule-capsule pair, and 2.68 for potassium for ampoule-syrup, are interesting to note. The latter value indicates that, among the liquid

Table 4
Statistical data related to the comparison of levels of macroelements in the different types of preparation. (Multiple comparison)

Pharmaceutical preparation	Macroelements			
	Sodium (*z* stat)	Potassium (*z* stat)	Calcium (*z* stat)	Magnesium (*z* stat)
Tablets–Ampoules	2.05*	1.81	2.20	2.63**
Tablets–Capsules	0.55	0.08	0.87	0.63
Tablets–Syrups	0.88	0.95	0.87	0.79
Ampoules–Capsules	2.56*	1.73	3.00*	2.05*
Ampoules–Syrups	1.98	2.68**	1.39	1.90
Capsules–Syrups	0.63	1.03	1.74	0.16

* > 2–2.64 $p = 0.10$; ** > 2.64 $p = 0.05$.

preparations, there was only a significant difference between K levels found in ampoules and syrups. Low z stats were obtained for the four elements in the tablet-capsule combination, suggesting a lower variability in range of values.

4. Conclusions

1. The macroelements sodium, potassium, calcium and magnesium were detected in significant quantities in the four different preparations although levels showed a high degree of variability.
2. Highest sodium levels were found in samples CA.2 and SY.3 (250 mg % and 183 mg %, respectively). Lowest sodium levels were found in the three ampoule samples.
3. Potassium was generally found in larger quantities than sodium in the 15 samples but showed great variability between samples.
4. Calcium was the major element found in the solid formulations. This was not true for the ampoules and syrups which showed values similar to sodium and reflected similar variability.
5. Largest amounts of magnesium were found in the solid preparations with largest amounts recorded in the capsules and lowest amounts in the liquid preparations, especially ampoules. The latter showed a particularly narrow range of values, i.e. from 2.50 mg % for AM.3 to 3.00 mg % for AM.1.
6. The lowest level of significance, $p = 0.0206$, corresponded to calcium, indicating the high degree of variability of this element in the 15 samples.
7. Multiple comparison of the results, taking into account every possible pair of combinations between the four types of preparation, showed that most significant variability occurred in combinations involving ampoules.

As a final consideration, it may be stated that propolis provides discrete quantities of these macroelements and may be used as a dietary supplement. The formulations tested in the present study contained several ingredients, often including essential oils which potentiate the action of this hive product and has applications in other medical fields.

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