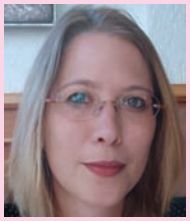

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Antioxidative/anti-ageing skin care products:
marketing claims or reality?

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ABSTRACT: As more and more anti-ageing and antioxidant skin care products flood the market, there is growing concern about definitions and experimental proof of effectiveness. Herein we present the antioxidative power of active ingredients and selected finished market products, with the objective of detecting the state of the art of modern cosmetics on the market. The results were disappointing. 30 market products that claim antioxidative properties were analyzed; 73 percent showed no or very low antioxidative activity. Encouraging enough, 13 percent showed very high values of Antioxidative Power (AP), proving that it is possible to create cosmetic products with a high content of antioxidative actives. The choice of the right actives, their stability and synergistic effects should be evaluated carefully in order to optimize the products and to fulfil the customer's requirements of analytical data that actually proves that these products are effective.

INTRODUCTION

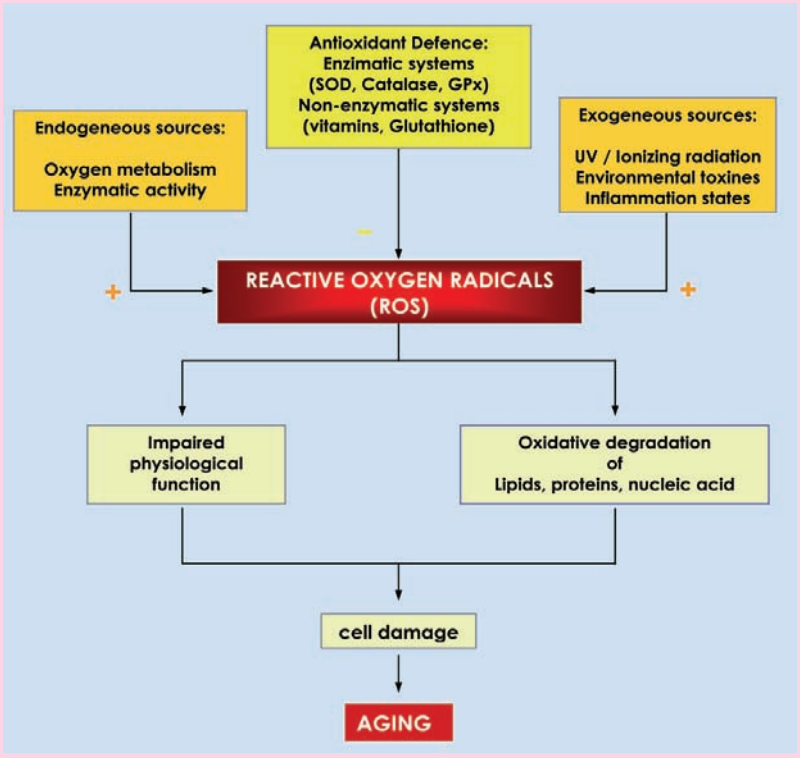
The need of effective anti-ageing skin care

We are finding more and more antioxidants present in our skin care products these days. The idea behind is to defend the skin against environmental stress that can severely damage our skin by oxidizing and deteriorating our cells, in the form of free radicals. Indeed, free radicals and specially reactive oxygen species (ROS) are generated in the skin in consequence to external stress (i.e. UV radiation, toxins, inflammation) or internal stress (inflammation, metabolic activity) (1). The biological consequences of an overloading amount of free radicals in the skin are manifold: wrinkling, photo ageing, elastosis, skin drying and pigmentation (2). Healthy skin is rich in an intrinsic antioxidative defence system aimed to reduce the amount of free radicals. In old skin or under oxidative stress this defence system becomes more and more pauperized and the external supply of antioxidants (topically or systemically) could be helpful to prevent skin ageing. Antioxidants fight free radicals and may neutralize therefore the primary physical agent that can lead to biological skin dysfunction (Scheme 1).

Requirements for antioxidants and formulations

The antioxidant strategy for cosmetics can be successful if several parameters and preliminary conditions are considered:

a) The antioxidants used should have a very high antioxidative capacity and reactivity in order to neutralize the very short time living ROS in the skin.
b) The antioxidants used should not be converted into reactive radical species themselves to avoid further radical chain reactions (i.e. ascorbyl radical, tocopheryl radical).
c) The antioxidants used should be sufficiently stable inside a cosmetic formulation without reacting and should be protected from oxygen in order to avoid changes in their oxidation status (i.e. polyphenols).
d) The lipophilic or hydrophilic character of antioxidants determines the distribution inside the skin tissues and



Scheme 1. Role of reactive oxygen radicals in biological systems.

makes them more or less accessible to free radicals.

e) The cosmetic formulation may enhance or hinder the penetration ability of actives inside the skin. The penetration depth, the amount of antioxidant molecules, the penetration velocity are particularly determined by the cosmetic formulation. The presence of emulsifiers or carrier systems, the type of emulsion (O/W or W/O), the amount of lipid components are some of the manifold factors that can influence the penetration kinetics of actives.

The need to consider all these influencing parameters reflects the complexity of antioxidative reactions and makes the creation of an efficient antioxidant cosmetic product a task of outstanding complexity (3).

Substance	AP (AU)	t_r (min)
Ascorbic acid *	1.000.000	0,24
2-phospho-ascorbic acid *	11.174	2,42
Ascorbyl palmitate *	430.000	0,24
α-tocopherol *	404.000	0,33
Tocopherol acetate *	0	-
Caffeic acid *	2.032.900	0,16
Caffeine *	0	-
Theobromine *	0	-
Aspalathin *	1.531.000	0,22
Ellagic acid *	1.352.000	0,60
Rosmarinic acid *	971.200	0,51
Coenzyme Q10 (ox)	1.600	0,17
Green Tea Extracts		
1.	3.677.360	0,14
2.	26.100	0,38
3.	6.215	0,51
4.	750.000	0,41
5. *	375.950	0,71

* purchased from Sigma-Aldrich at the highest purity grade available.

Table 1. AP values and reaction times of several antioxidants used for cosmetic products.

To create skin care products having a verifiable effect against free radical injury, it is necessary to prepare skin care products that contain sufficient high doses of antioxidants and that deliver them into the living layers of the skin. To be efficient against free radicals, an antioxidant has to be able to neutralize free radicals where they are formed, mainly in the epidermis and dermis. A first step towards functional antioxidant cosmetic is to formulate emulsions with a high active concentration. The choice of the right active components is of crucial importance. Considering only the European market, there are more than 2000 different actives used for cosmetics with antioxidative / antiageing claims. The decisions of which antioxidants are used are often affected by marketing requirements more than by scientific evidences. In 80 percent of all products, the consumers request for "vitamin E" is satisfied by the use of tocopherol acetate, a stabilized form of tocopherol, which is completely inactive and is not to be considered an antioxidant (4). The same is true for "vitamin C", where stabilized forms of ascorbic acid are used that have very reduced antioxidative activity. Other "trends" in the anti-ageing market result in likewise ineffective products. Hundreds of skin care products contain "Coenzyme Q10". Q10, in its ubiquinone reduced form is an efficient antioxidant and it is a very expensive raw material. The oxidized ubiquinolic form is significantly cheaper and is used for all cosmetic preparations, but it is no longer able to reduce free radicals because its oxidative status changes. Inside the skin the oxidized form may be converted into the active reduced form and the enrichment of the mitochondrial ubiquinone pool has certainly beneficial physiological effects, but the primary function as a radical scavenger is surely lost!

Natural botanical extracts are more and more frequently found in skin care and are claimed to be efficient against free radical injury. Most of them are polyphenolic compounds extracted from a huge variability of plants with different extraction techniques. Tea extracts (Canellia sinensis), exemplarily for all polyphenolic compounds, are probably the most common ingredients in modern cosmetics and the customers associate beneficial anti-ageing and antioxidative claims with green tea. An unfermented green tea extract has a very high antioxidative activity and at the lowest oxidative status one polyphenolic molecule may capture up to 4 electrons derived from free radicals. At higher oxidative states, thus when fermentation takes place, the antioxidative activity decreases dramatically. Oxidative fermentation may occur beginning from the raw material over the production process and the storage. The final product (extract) often is not stable inside a cosmetic emulsion and will loose its activity in a very short time.

Antioxidative Power (AP) – a uniform tool for the quality control of raw materials and final products

These few examples demonstrate the need of a uniform tool able to describe the antioxidative properties of active ingredients as well as final cosmetics in order to create efficient products. The choice of the right antioxidants is only the first step in this direction, but also the most important. The analytic method should be able to quantify the antioxidative activity towards free radicals in the active (liquid or solid, lipophilic or hydrophilic) or in a mixture of active compounds and in the final cosmetic formulation (emulsion). The method Antioxidative Power (AP) is an ESR based analytical tool that fulfils these requirements (5-8). This new 2D parameter Antioxidative Power (AP) enables to characterize a substance or mixture regarding its capacity to remove a certain number of free radicals in a certain time interval. Thus, both the reactive capacity and the reaction velocity are considered. Especially the reactivity is typical for each antioxidant class and can help to identify the main active antioxidant in a mixture or to make a point on the oxidative status of polyphenols.

product	Prize category	AP (AU)	t_r (min)
1	L	0	--
2	L	0	--
3	L	0	--
4	L	0	--
5	L	0	--
6	L	0	--
7	H	0	--
8	H	0	--
9	H	9	6,7
10	H	9	2,65
11	L	11	0,49
12	H	13	1,41
13	H	16	1,23
14	H	18	2,15
15	H	20	1,92
16	H	24	1,36
17	L	32	0,48
18	L	34	1,38
19	L	43	0,24
20	L	51	0,9
21	H	56	3,0
22	L	66	0,27
23	L	217	0,3
24	L	220	0,24
25	H	256	0,28
26	H	402	0,31
27	H	19160	0,24
28	H	22327	0,33
29	H	46644	0,24
30	H	54615	0,24

Table 2. AP values and reaction times of market products. All tested cosmetic products had the claim "contains antioxidants and/or vitamins".
High prize [H] (>15 € / 50 mL) and low prize [L] products (< 15 €/ 50 mL) have been analysed.

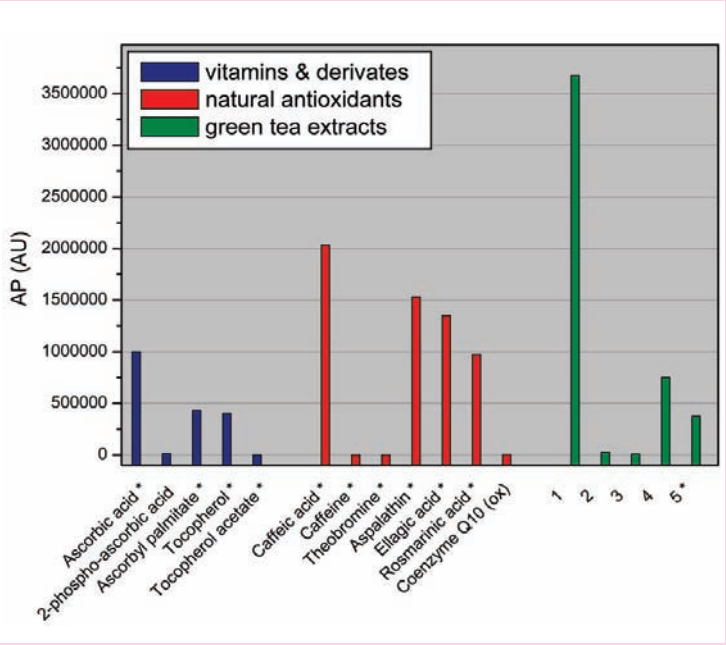


Figure 1. AP values of several antioxidants used for cosmetic application.

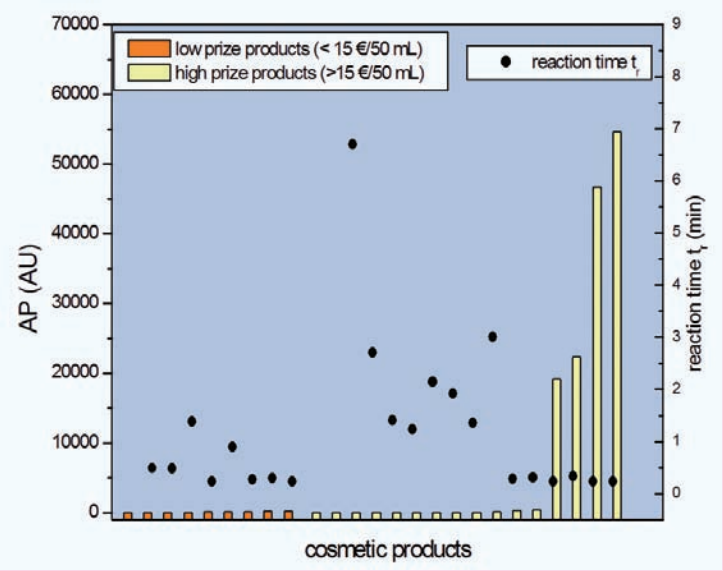


Figure 2. AP values and reaction times of market products. The bars indicate the Antioxidative Power expressed in Antioxidative Units (AU); the scatter data refer to the reaction time tr.

The method is standardized and benchmarked to ascorbic acid and is expressed in Antioxidative Units (AU), where 1 AU corresponds to the activity of 1 ppm ascorbic acid according to:
AP (1 ppm ascorbic acid) = 1 AU = 2.495 10^{13} spins/mg*min
The benchmarking allows to compare the activity of very different classes of antioxidants.
With the help of this tool we have determined the antioxidative activity of raw materials as well as final market products that claim antioxidative/anti-ageing activity.
The aim of this study was to select the most efficient raw materials and to elicit the "state of the art" of modern cosmetics on the market.

Results 1: AP values of active ingredients

The Antioxidative Power and reaction times (t_r) of widely used raw material with antioxidative claims used for cosmetic application are reported in Table 1 and Figure 1.
Every stabilisation of ascorbic acid and tocopherol results in a dramatic reduction of the antioxidative capacity. Natural extracts, i.e. green tea extracts, are affected by a very high variability. Also the long term stability differs between different extracts and even between different batches of the same extract (data not shown).
With this basic information it is possible to anticipate the Antioxidative Power of final products knowing only the INCI-list.

Results 2: AP values of cosmetic products

We tested 30 market products that claim: "contains vitamin C and/or E", "antioxidative effect", "anti-ageing effect", "radical scavenging" and that contain at least one antioxidant in the INCI list. As a result we obtained disappointing low AP values in the major part of the products. The AP values and reaction times are reported in Table 2 and Figure 2.

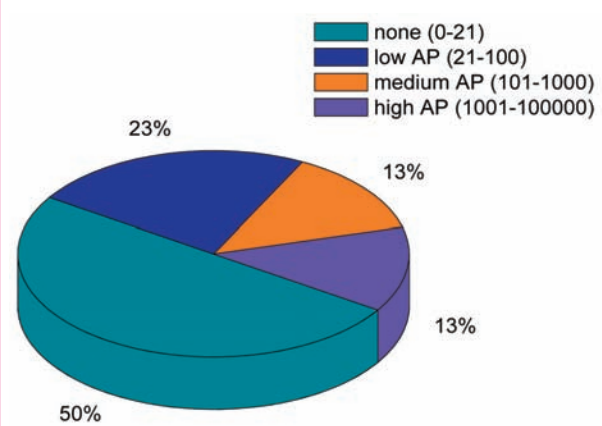


Figure 3. Distribution of the products having AP values in segments of none, low, medium, and high values.

For 73 percent of the tested products none or a very low antioxidative power was attested, independent on the prize category. Only 13 percent showed very high antioxidative activity, indicating that it is possible to obtain stable and effective antioxidative skin care products. All of these excellent performing products belong to the high prize segment.
In Figure 3 the results are represented for categories of low, medium, and high AP values.

CONCLUSION

Skin care products with antioxidative claims are one of the most fast growing market for cosmetics worldwide. Despite this fact, there are many products with no or very low antioxidative activity. The choice of the right active compounds, the verification of their activity inside a cosmetic formulation, their stability and synergistic effects should be the first step toward the creation of modern and effective products. To be active inside the skin, the antioxidants have to penetrate into the living layers of the skin, where free radicals are generated and should be effective against ROS. This is possible only if the topical applied formulation holds the potential to be effective. Marketers seeking to create impact with performance should use Natural ingredients as antioxidants as a key element of their marketing strategy in cosmetics and toiletries, considering the need of analytical data that actually proves that these products are effective.

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