Antioxidative Skin Care Products : Marketing Claims or Reality?

K. Jung, M. Seifert, Th. Herrling

Gematria Test Lab GmbH – Pestalozzistr. 5-8, 13187 Berlin, Germany

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Introduction

As more and more anti-aging and antioxidant skin care products flood the market, there is a growing concern about definitions and experimental proof of effectiveness. The expanding range of natural actives in mainstream cosmetics is the proof that the industry now relies heavily on these ingredients. “Natural” is the biggest trend and one of the fastest growing segments in Cosmetics, with $ 7 billion and double digit growth. The demand of cosmeceutical products is expected to increase to more than $ 8 billion by 2010 (1).

Most of the cosmeceutical actives target antiaging efficacy, and since most antiaging efficacy deals with antioxidative activity, the activity of market products against free radicals is one of the most important claims. The idea behind is to defence 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 especially 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) (2). The biological consequences of an overloading amount of free radicals in the skin are manifold: wrinkling, photoageing, elastosis, skin drying and pigmentation (3). Healthy skin is rich in an intrinsic antioxidative defence system aimed to reduce the amount of free radicals. In elder 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 agent that can lead to biological skin dysfunction. More and more consumers and producers are becoming aware of the relationship between food, health and appearance. This is caused by the intersection areas of nutricosmetics, supporting beauty from inside, and cosmeceuticals, supporting health from the outside. Indeed, many natural actives common in the food and food supplement industry are entering the cosmetic market. Well known examples in the last few years are carotenoids, coffee, tea, grape, melon, pomegranate, apple, various “super-fruits”, among many others. The conclusion that healthy benefits for the skin could be taken from physiological healthy food is reasonable, at least for the antioxidative properties (4).

The objective of this work was to detect the state of the art of modern antiageing cosmetics claiming their activity against free radicals. The analytical method used was the detection of the Antioxidative Power (AP) (5-7). The results were disappointing: 37 market products that claim antioxidative properties were analyzed: 73 % showed no or very low antioxidative activity (Fig. 1). Encouraging enough, 13 percent showed very high values of Antioxidative Power (AP), proving that it is possible to create cosmetics with 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.

For this purpose, several extracts have been analyzed and compared. Exemplary for natural extracts we have chosen green tea (*Camellia sinensis*), pomegranate (*Punica granatum*), artichoke (*Cynara scolymus*), and rosemary (*Rosmarinus officinalis*). Among each phytoextract we found a variability of 500-600 fold in the antioxidative capacity and reactivity. In some cases oxidation or fermentation processes had altered the final product; in other cases the concentration in antioxidative actives is quite low. If efficacy is the major objective, raw materials should be chosen in order to obtain a final cosmeceutical product with high Antioxidative Power (AP).

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. The cosmetic formulation may enhance or hinder the penetration ability of actives. The penetration depth, the amount of actives that reaches the epidermis, and 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.

To demonstrate this influence on the performing characteristics of antioxidants inside the skin, one active was selected (a pomegranate extract), and different cosmetic formulations were prepared containing 1 % of this extract. The determination of the Skin Antioxidative Retention (SAR) is an adequate tool to detect both the penetration kinetics and the antioxidative / free radical scavenger activity inside skin biopsy samples (8,9).

Results and Discussion

Green tea extracts (fig.2a):

7 green tea extracts have been analyzed. The results show amazing differences in the antioxidative performance ranging from 3.600.000 AU to 6.200 AU. This corresponds to differences up to 580 fold. The reaction times indicate the oxidation state of the polyphenols; the higher is the reaction time, the lower is the reactivity of the antioxidants towards free radicals. Reaction times higher than 0,45 min indicate that fermentation (oxidation) processes or in the raw material or during the production process or storing have been taken place. One of the seven extracts presented a high reaction time of 0,77 min; the remaining 6 extracts showed lower reaction times, indicating that real green tea (and not fermented black tea) was used. The main antioxidants present in *Camellia sinensis* are epigallochatechines and

various polyphenolic compounds. The colours of the extracts varied from dark green to pink-orange.

Rosemary extracts (fig. 2b):

The results of the rosemary extracts showed a lower variability, ranging from 40.320 AU to 243.500 AU. There are differences in the activity of “only” 6 fold. With respect to the green tea, the rosemary extracts presented higher variability in the reaction times, ranging from 0,24 min to 0,75 min. The reaction time of pure rosmarinic acid, was determined to be 0,51 min; higher reaction times indicate oxidation, lower reaction times indicate the addition of antioxidants as ascorbic acid.

Artichoke extracts (fig. 2c):

Different to the former two extracts, the artichoke (Cynara scolymus) is not yet used for cosmetic application. The presence of high contents of chlorogenic acid, a potent antioxidants present also in coffee beans, makes it a potential candidate for cosmeceutical application. The activity of chlorogenic acid (pure substance) was determined to be 460.300 with a reaction time of 0,3 min. One of the four tested extracts presented a low reaction times, indicating high content in chlorogenic acid. Also polyphenols with higher reaction times are present in the artichoke extracts. The results show a high variability, ranging from 850 AU to 420.600 AU, corresponding to differences in the activity of 490 fold.

Pomegranate extracts (fig. 2d):

Rich in polyphenols as ellagic acid and punicalagin (tannin), the pomegranate extract is often used for both nutraceutical and comsmeceutical application. Ellagic acid is one of the most potent polyphenolic antioxidant with 1.352.000 AU and 0,60 min. reaction time. As for the other extracts, we found a huge variability: the AP results ranged from 1.940 AU to the 365 fold more active extract with 709.560 AU. The seed oil has the lowest Antioxidative Power with 570 AU. Polyphenols, anthocyanins, and other tannins in the fruit pulp and the fruit rind are responsible for the outstanding antioxidative performance of pomegranate products.

One of the pomegranate extract was chosen for the preparation of three different cosmetics: two oil-in-water formulations (O/W 1 and O/W 2) and one water-in-oil formulation (W/O). The Antioxidative Power (AP) was determined after 10 days storage at 40℃ and the recovery of the antioxidati ve activity was found to be 90-100 %. These formulations were applied on skin biopsy samples at 2 mg/cm2) for 15 minutes, the skin was exposed to UV radiation (0,5 MED using a sun simulator) to generate free radicals and the Skin Antioxidative Retention (SAR) was determined for each of the three cosmetics (Fig. 3). The best results were obtained with the light O/W 2 formulation (Unguentum emulsificans aquosum), where the formulation protects against 86 % of the UV induced free radicals. No or only slight retention of the Antioxidative Power of the skin was measured for the O/W 1 formulation (Cremor basis) and for the W/O formulation (Lanae alcoholum unguentum).

This study demonstrates that the creation of a cosmetic preparation with high antioxidative properties is a target of outstanding complexity. Three main milestones have to be considered: 1) the choose of an adequate antioxidative raw material (activity); 2) the incorporation of this active inside a cosmetic formulation and the verification of the Antioxidative Power also after severe storing conditions (stability); 3) the penetration ability and efficacy of the antioxidants inside the skin (performance). 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 (9). This is possible only if the topical applied formulation holds the potential to be effective.

References

(1) Research Studies-Freedonia Group http:/www.allbuiseness.com/marketing/market-research/3948712-1.html 04/2009.

(2) B. Halliwell, B.C.J. Gutteridge. Free radicals in biology and medicine, 3rd editione, Oxford University Press (1999).

(3) T.M. Callaghan, K.P. Wilhelm. “A review of aging and examinatione of clinical methods in the assessment of aging skin. Part I: Cellular and molecular perspectives of skin aging”, Int. J. Cosmet. Sci. 30(5), pp. 313-322 (2008).

(4) Trommer H, Neubert RH. Overcoming the stratum corneum: the modulation of skin penetration. A review. Skin Pharmacol Physiol.19(2):106-21, 2006.

(5) Jung K, Richter J et al. The antioxidative power AP – a new quantitative time dependent (2D) parameter fort he determination of the antioxidant capacity and reactivity of different plants. Spectrochim Acta A Mol Biomol Spectrosc. 63, 846-50, 2006.

(6) Jung K, Sacher M et al. Anti-Aging status of skin characterized by the Skin Antioxidative Protection (SAP)-efficacy of topically applied antioxidants. SÖFW Journal 132 (9), 33-44, 2006.

(7) Jung K, Herrling Th. Insights in the role of antioxidants in modern skin care and hair care products – methods to prove their activity. Global Ingredients & Formulation Guide 2007. Verlag f. chem. Industrie, Augsburg, Germany, 197-215, 2007.

(8) Jung K, Seifert M, Herrling Th. Antioxidative / anti-aging skin care products: marketing claims or reality? H&PC today, n1/2009, 37-40, 2009.

(9) Jung K, Sacher M, Blume G, Janssen F, Herrling Th. How active are biocosmetic ingredients? SÖFW Journal 133 (1/2) 2-7, 2007.

Figures

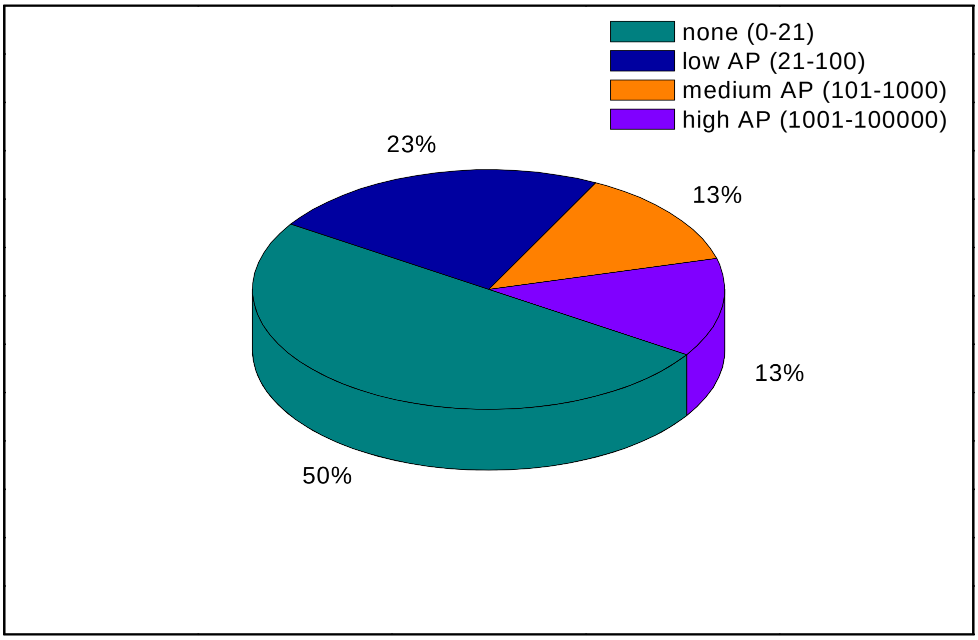
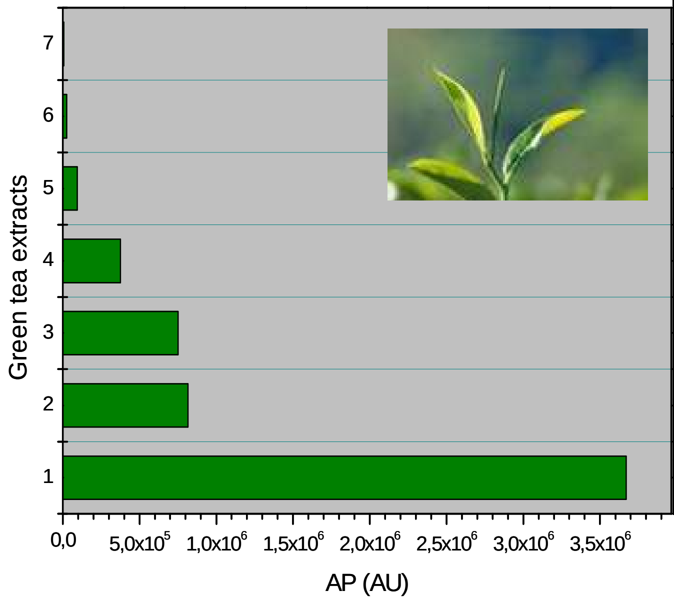


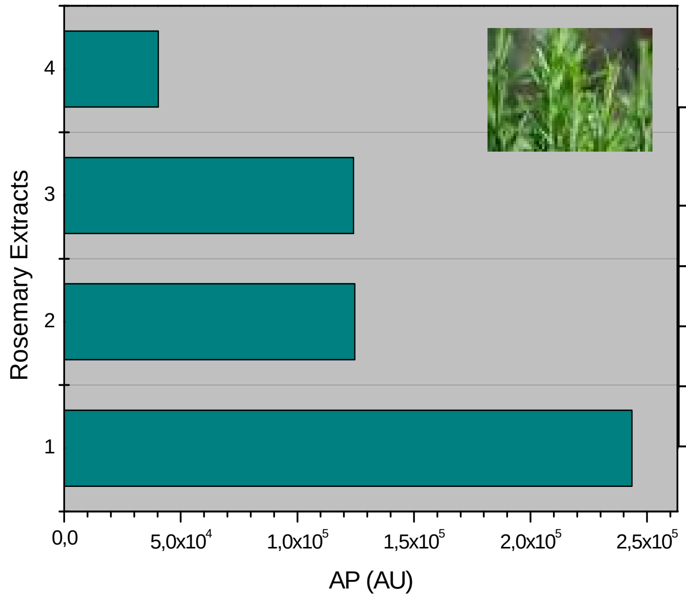
Fig. 1 Screening of the Antioxidative Power (AP) of 37 market products claiming antioxidative properties.



Green Tea extracts
Camellia sinensis

Extract	AP (AU)	t_r (min)
1	$3,67 \times 10^6$	0,39
2	815149	0,44
3	750000	0,41
4	375950	0,39
5	95229	0,36
6	26100	0,77
7	6215	0,41

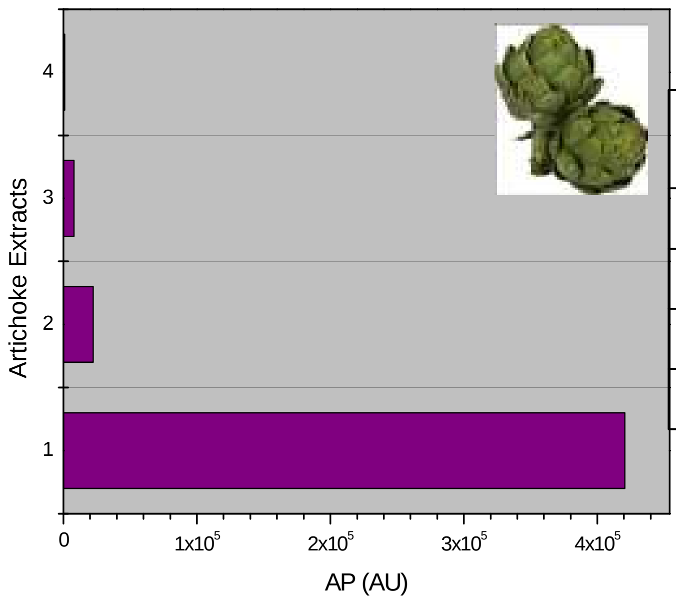
Fig. 2a. AP values and reaction times (t_r) of seven different green tea extracts



Rosemary extracts
Rosmarinus officinalis

Extract	AP (AU)	t_r (min)
1	243500	0,75
2	124712	0,38
3	124126	0,24
4	40326	0,68

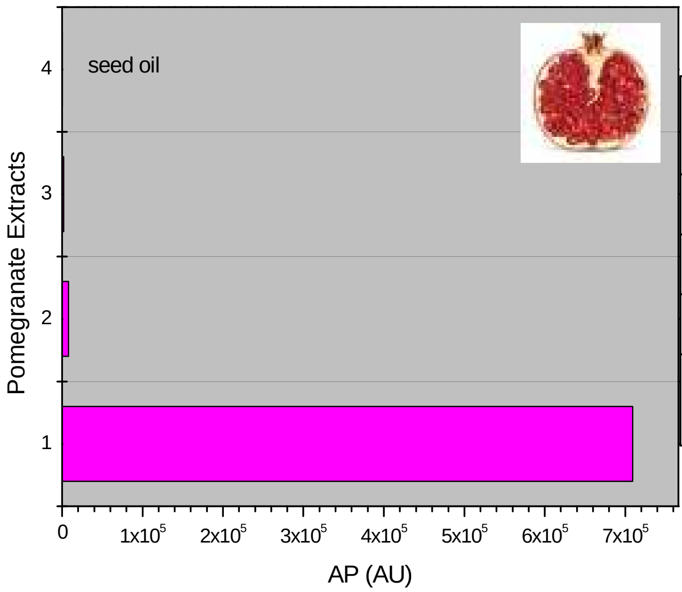
Fig. 2 b. AP values and reaction times (t_r) of 4 different rosemary extracts.



Artichoke extracts
Cynara scolymus

Extract	AP (AU)	t_r (min)
1	420600	0,21
2	22299	0,69
3	8019	0,67
4	854	0,75

Fig. 2 c. AP values and reaction times (t_r) of 4 different artichoke extracts.



Pomegranate extracts
Punica granatum

Extract	AP (AU)	t_r (min)
1	709567	0,40
2	8012	0,77
3	1940	0,75
4	570 (seed oil)	0,53

Fig. 2 d. AP values and reaction times (t_r) of 3 different pomegranate extracts and one seed oil.

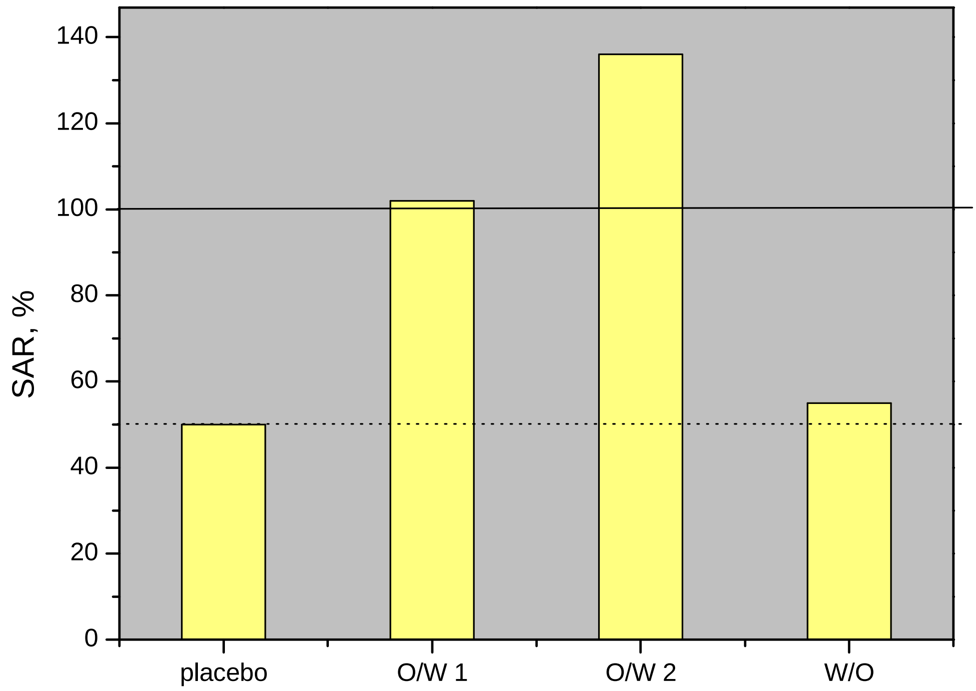


Fig. 3 Skin Antioxidative Retetion (SAR) for three cosmetic formulations containing 1 % of pomegranate extract applied for 15 minutes.