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Extending the shelf life of cosmetic products through novel stabilisation of exotic butters and oils

Keywords: Internally stabilised, rosemary extract, exotic butters

Introduction

Application of various oils and other natural materials for skincare or religious purposes is an ancient practice. With advent of time, the range of cosmetic products has developed in a rapid pace and during modern times, the consumer market is flooded with innumerable skincare products. But whatever be the type of product or branding, presence of a lipoid material ties the modern day formulations to the ones of the ancient times.

One of the principal reasons for use of a lipid material in cosmetics is its emolliency. The term »emollient« is of Latin origin meaning a material capable of smoothening dry and wrinkled skins and maintaining these conditions for a certain period of time. Water alone is capable of exhibiting such effects but the effects are short lived due to its quick evaporation. A cream, lotion or moisturizer (can be oil in water emulsions and vice versa) is designed to give visual smoothening effect on a dry skin immediately after application. This is due to its ability to hydrate the skin and modify the physical and chemical nature of the skin surface. The ability of the lipid to form a film on the skin surface which delays the evaporative loss of water when the emulsion dries, is termed occlusivity. The intercellular spaces between the partly desquamated skin fragments are filled up immediately after the application of the moisturizer and the surface becomes very regular (friction is greatly minimised), giving rise to a smooth and shining look of the skin. The gloss imparts a rich look to the skin (1).

Presence of essential fatty acids (EFA) like, linoleic acid (n-6), α-linolenic acid (n-3), γ-linolenic acid (n-6) in the oils is often an important criterion for selection. Effect of such EFA's on human physiological systems through oral intake is well documented. They also contribute to beneficial physiological activities when applied topically through creams or lotions.

Both natural oils and exotic butters are widely used in cosmetic products and neutraceuticals (2). Evening primrose oil (EPO) (*Oenothera biennis*) and borage oil (*Borago officinalis*) are very common natural oils, used primarily because of their high content of gamma linolenic acid. Evening primrose oil and borage oil contains about 9-11 % and 18-23 % of gamma linolenic acid respectively. Use of oils with high amount of polyunsaturated fatty acids like camelina oil (*Camelina sativa*), blackcurrant seed oil (*Ribes nigrum*) and flax seed oil (*Linum Usitatissimum*) for cosmetic applications are also prevalent. Usually obtained from tropical jungle crops, exotic butters like shea (*Butyrospermum Parkii*), mango (*Mangifera indica*), sal (*Shorea robusta*) are among the commonly used exotic butters for skin care products. They are rich in symmetrical monounsaturated triglycerides which are solid or semi-solid at room temperature. They have narrow melting points and have appreciable viscosity and emulsion stability. The exotic butters are also rich in unsaponifiables such as sterols, ubiquinones, fatty alcohols, fatty esters, triterpines etc (3). Application of natural oils and butters in various cosmetic formulations is a great challenge in combating oxidation.

Oxidation of oils and fats

The oil or fat content of a cosmetic product can vary from 2-15 % in case of body lotions and creams while it can be 100 % in case of massage oils. It is very important that only the best quality oil or fat is used in any cosmetic formulation. »Quality« of a commercial oil or fat is very often measured through its oxidative stability. Oxidation of a lipid is a very common and serious problem for any fat containing product, food or cosmetic. Characteristic changes linked with oxidative degradation of oils and fats include development of malodors, unpleasant tastes and might lead to change of colour, increase in viscosity, specific gravity and solubility. The mechanism of autoxidation has postulated by many authors (4, 5, 6,). Autoxidation is a natural free radical process between molecular oxygen and the unsaturated fatty acids of an oil which leads to the formation of short lived hydroperoxides (primary oxidation products). The hydroproxides readily break down to form alcohols, aldehydes, ketones and other hydrocarbnons. These secondary oxidation products impart rancid odor and taste (7). One way of preventing autoxidation is addition of antioxidants.

The interest of the food and cosmetic industry in phenolic antioxidants is primarily related to the extension of the shelf life of the various consumer products. In the present global market, there is hardly any food or cosmetic product, semi-finished or finished, which does not contain any added preservatives. The antioxidants used are mostly synthetic, namely butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), ascorbyl palmitate, tertiary butylhydroxyquinone (TBHQ) etc. But the consumers' awareness of the possible toxic side effects of synthetic antioxidants and preference for natural additives, has led to more detailed investigations and applications of natural herb extracts as antioxidants.

This paper highlights two highly efficient ways of stabilising oils and butters without application of synthetics. Using supercritical CO_2 and other solvents like ethanol for extraction, the components of rosemary extracts (*Rosmarinus officinalis*) have been well studied. The composition of rosemary extract is quite complex, consisting of a mixture of phenolic acids and diterpenes (8). The main antioxidative ef-

fect of Rosemary extracts come from three phenolic compounds namely, carnosic acid, carnosol and rosmarinic acid of which over 90 % of the antioxidant activity is from carnosic acid and carnosol (9). Flavonoids, particularly, flavones have also been identified in rosemary extracts. Apart from the antioxidant activity, there are mentions of antimicrobial, antiviral, antimutagenic and anticarcenogenic activities of rosemary extracts (10).
Despite these various benefits, application of rosemary extracts often incorporate a distinctive flavour, characteristic of rosemary. This limits the use of rosemary extracts to a large extent in food and cosmetic products. Using rosemary extracts, International Cosmetic Science Centre (ICSC) have developed a process called »internal stabilisation« by which all exotic butters and natural oils are protected against oxidative deterioration. The butters and oils used for our study of internally stabilised products are Shea butter, Mango butter, Sal butter or Shorea butter, Evening primrose oil and Borage oil. Another way of protecting oils and butters is by external addition of Rosemary extracts. The oils and buters used for this are, camelina, flax, blackcurrant, evening primrose and borage and mango butter and shea butter.

Methods

Oil stability index (OSI) was determined as a tool to judge oxidation stability. The instrument chosen for determining OSI was Rancimat 679 from Metrohm Ltd, Switzerland. The principle of Rancimat analysis depends on the measurement of increase of electrical conductivity by the volatile carboxylic acids generated in the oxidising oil sample. The temperature was maintained at 120 °C for the exotics and 80 °C for Blackcurrant and flax seed oil and 100 °C for borage oil and camelina oil. The air in-flow was maintained at 18 lit / hr and the sample size was 3.5 ± 0.05 gm.

Results and discussions

a) Internal stabilisation
The data obtained, induction periods (IP) from the Rancimat tests were plotted as a function of time to obtain bar diagrams which show the relative increase of oxidative stability for each of the test samples. The results are divided into two groups, namely, the exotic butters and natural oils.

Exotic butters:
Fig. 1 shows the increase of oxidative stability of the internally stabilised exotic butters by varying degree.
The Rancimat value for the control (cntrl) sample of mango butter is 7.7 hrs. The same sample of mango butter when internally stabilised with Rosemary extracts, gives a Rancimat value of 20 hrs. This indicates a rise of stability by factor of 20.1 / 7.72 = 2.6. In case of shea butter, the internally stabilised sample, compared to control sample, shows a four fold increment from 3.4 hrs to 14.8 hrs. Internally stabilised sal butter has a Rancimat value of 18.5 hrs which is about twice that of the control sample of sal butter.

Natural oils:
The necessity of an anti-oxidant in natural oils is much more than in exotic butters. This is attributed to their high content of polyunsaturated fatty acids. The rate of oxidation increases many folds with every single addition of an unsaturation moiety in the fatty acid backbone. The internally stabilised evening primrose oil and borage oil show much higher oxidative stability index as indicated by Rancimat data. Plotting the Rancimat values as a function of time give a set of bar diagram as in **Fig. 2**.
There is a significant rise in oxidative stability of the internally stabilised oils. For evening primrose oil the Rancimat value shoots up from 11 hrs to 23 hrs while for borage oil it increases to 26

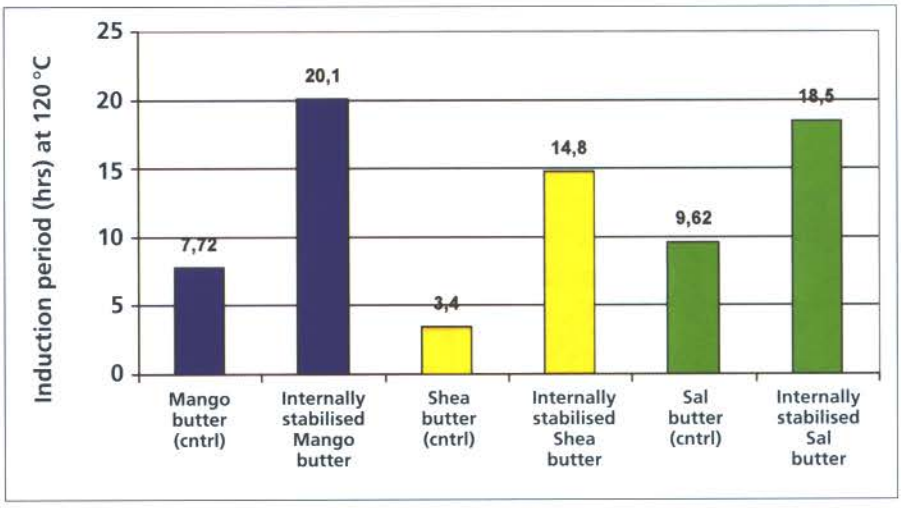

Fig. 1 Increase of oxidative stability of internally stabilised exotic butters

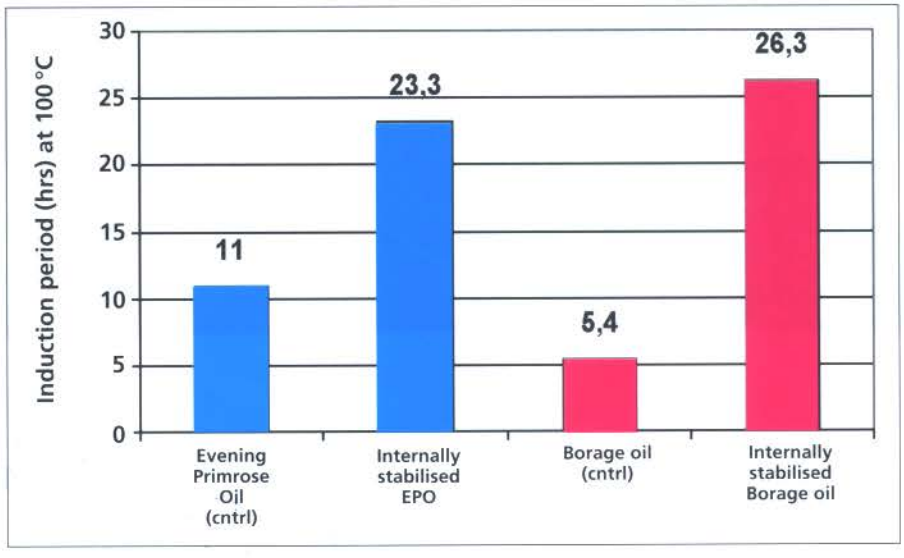

Fig. 2 Increased oxidative stability of internally stabilised natural GLA oils

hrs from 5.4 hrs. The two fold increase of stability for evening primrose oil and four fold increase in case of borage oil is a marked improvement.

b) External addition of Rosemary extracts

The Rancimat values or the induction periods (IP), in hours, for different oils were grouped together and plotted as bar diagrams for comparison vis-à-vis the control sample (cntrl) containing no Rosemary extracts. The two groups were, oils rich in polyunsaturated fatty acids (evening primrose, borage, flaxseed, blackcurrant seed, camelina) and the exotic butters (shea and mango).

To investigate the effect of varying dosages of rosemary extract as a natural antioxidant, evening primrose oil was selected as a guide. Dosages of 270, 510, 770 and 977 ppm were added to evening primrose oil and put to Rancimat analysis at 100 °C. The IP data were plotted as bar diagrams as in **Fig. 3**.

Fig. 3 shows a steady and progressive increase of oxidative stability of evening primrose oil with increasing dosage of rosemary extracts. The induction period of evening primrose oil increases almost linearly with increasing dosage of rosemary extracts. As the dosage increased from 270 ppm to 977 ppm, the induction period increased from 6.82 hrs to 9.53 hrs. The protection factor (IP of sample / IP of control) at 977 ppm is 9.53 / 6.62 = 1.43. It can be interpreted by protection factors that addition of about 1000 ppm of rosemary extracts into evening primrose oil increases the oxidative stability by approximately 40 %. This could be extrapolated to 200 % at ambient temperature of 20 °C thus providing extensive protection against oxidation.

Effects of rosemary extracts (1 000 ppm) on blackcurrant seed oil and flaxseed oil were observed from IP's at 80 °C **(Fig. 4)**.

Similar to evening primrose oil, blackcurrant oil and flaxseed oil also show improvement of oxidation stability on addition of rosemary extracts. IP of blackcurrant oil is increased to 38,5 hrs from 35 hrs while for flaxseed oil, one of the most important vegetable sources of omega-3 linolenic acid, addition of 1000 ppm of rosemary extracts increases its oxidative stability by a factor 32.4 / 25.8 = 1.25.

Borage and camelina oil also exhibit increase of oxidative stability due to addition of 1 000 ppm rosemary extracts **(Fig. 5)**. For borage oil, the IP is raised by about 25 % while camelina oil shows a 33 % rise in IP.

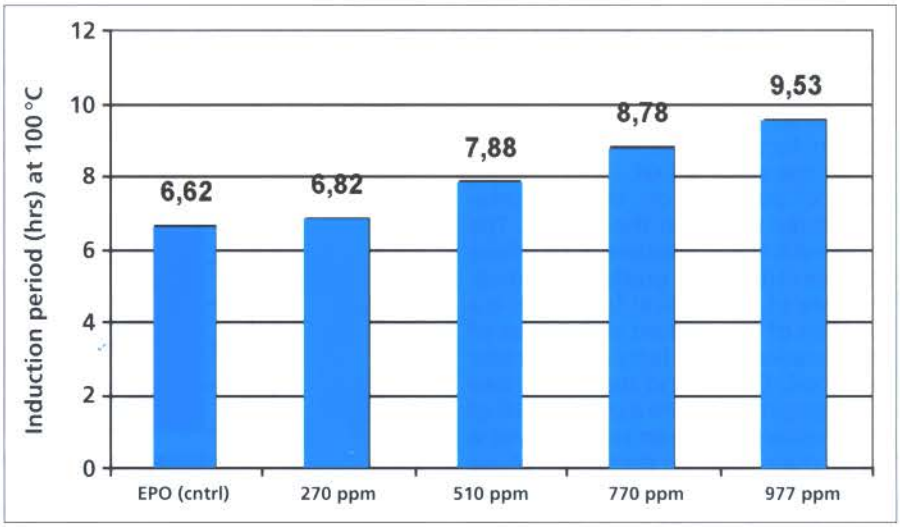

Fig. 3 Effect of rosemary extract on evening primrose oil

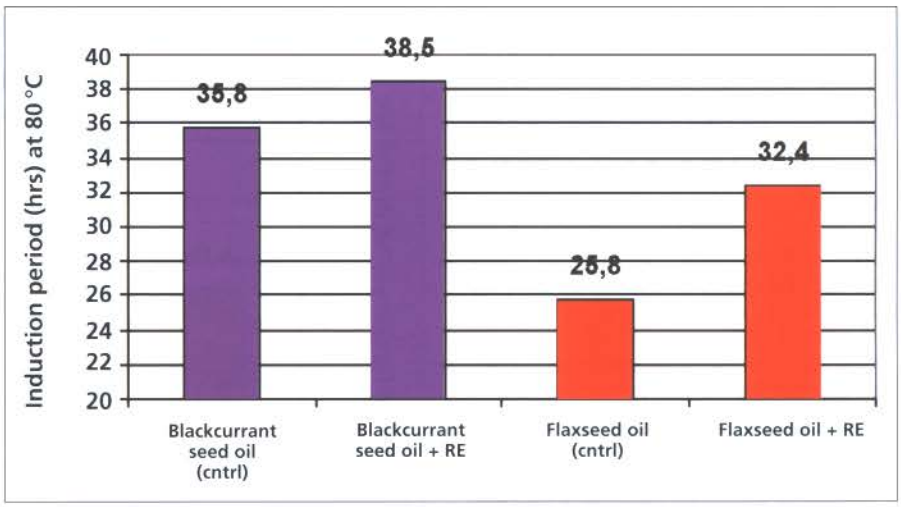

Fig. 4 Effect of rosemary extracts on blackcurrant oil and flax seed oil

Exotic butters:

By addition of rosemary extracts (1 000 ppm) the oxidative stability of exotic butters can be increased, the extent of which is dependant on the nature of the butter. **Fig. 6** shows the different levels of oxidative protection from rosemary extracts on shea and mango butter.

Addition of rosemary extracts has prominent effects on mango butter and shea butter. Mango butter containing Rose-

mary extract has an IP of 16.8 hrs (11.6 hrs for cntrl) while that for shea butter has of IP of 14.9 hrs (9.08 hrs for cntrl). Thus, addition of 1000 ppm of rosemary extracts in mango butter gives a protection factor is 1.45 while for shea butter the value is 1.64.

Classical autoxidation theory postulates three phases in the process. The first step is the »initiation« step where the free radicals are gradually formed. The rate of free radical formation is a function of the amount and degree of unsaturation of the fatty acids present in the oil. The second step is the step of propagation where a critical level of free radicals has been reached and a faster chain reaction starts. This phase is marked by rapid absorption of oxygen with the formation of peroxides. The third phase, termination, involves the recombination of the various species of free radicals and thus there is a decrease of the rate of oxidation. But, by this time, a substantial extent of oxidation has already taken place and the oil is completely rancid. The time period between the initiation and propagation is called the »induction period« and longer is this time period, greater is the oxidative stability of the oil.

Induction period correlates closely with the onset of rapid absorption and notable deterioration of flavour. They can thus be measured most directly by determining absorption of oxygen as a function of time.

From all the induction period data obtained by Rancimat tests, we see a marked on increment in oxidative stability of the test samples compared to control samples. This is due to the antioxidative effect of Rosemary extract. The mixture of diterpene alcohols present in Rosemary extracts act as natural antioxidants and prevents oxidation. The oxygenation of the free radical from the fatty acid of the lipid to form the lipid peroxyl radical is very rapid. Carnosic acid and carnosol, the main active ingredients of rosemary extracts are effective radical scavengers for peroxyl radicals, the primary product of autoxidation and interrupts the propagation steps. In turn they form antioxidant radicals of very low activity inactivating any further reaction with lipids. It has been shown (11) that the molecules of carnosol and the radicals generated from them participate in the reactions of chain initiation and propagation to a much lower degree compared to most natural and synthetic antioxidants.

Presence of an antioxidant in an oil or fat cannot prolong the oxidative stability for ever. Under strong oxidising conditions, the antioxidants are soon used up and the gradual lowering of

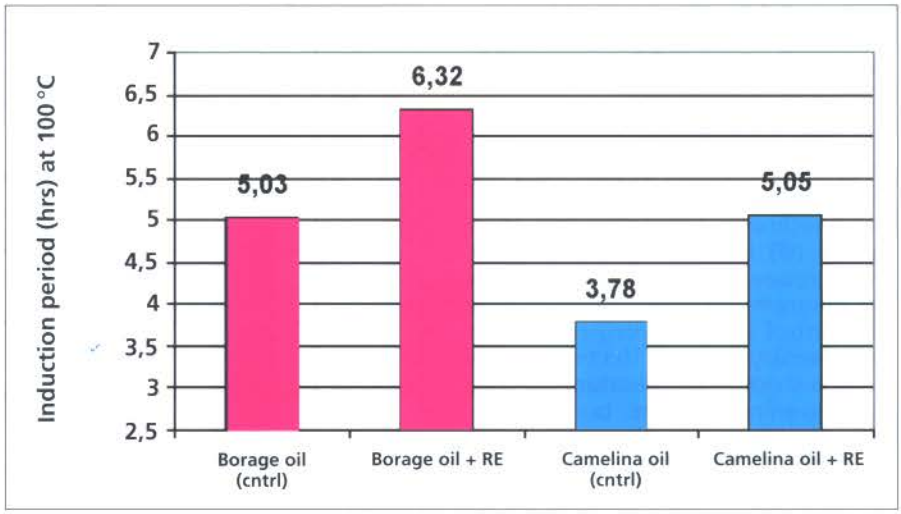

Fig. 5 Effect of Rosemary extracts on Borage and Camelina oil

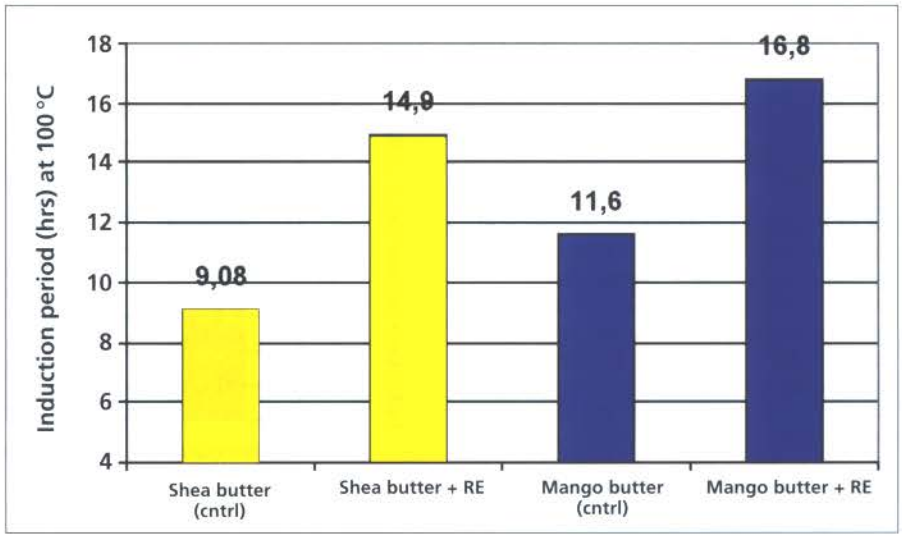

Fig. 6 Effect of rosemary extracts on exotic butters

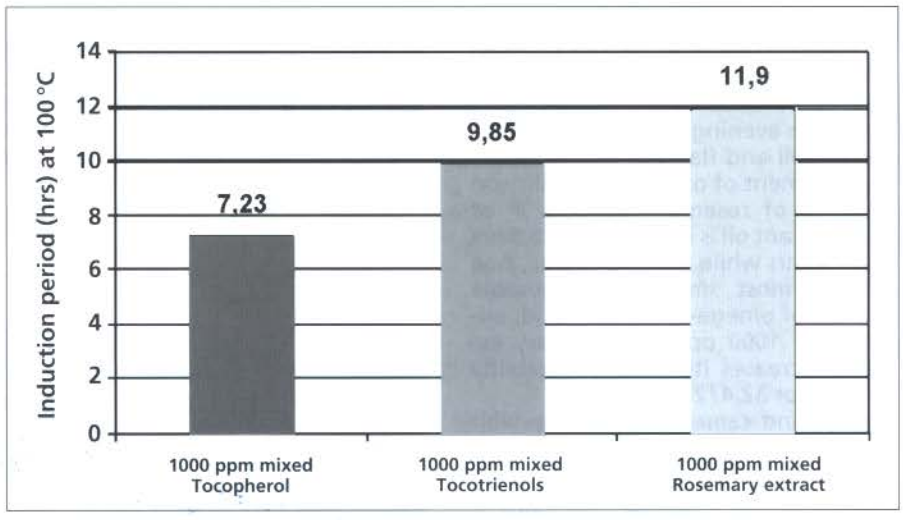

Fig. 7 Comparative effect of Rosemary extract and other natural antioxidants in EPO

their concentration enforces rancidity. Thus, higher values of induction period, at any given temperature, reflect the longer time taken by the sample to develop rancidity. In fact, the temperatures used for accelerated tests are far from standard storage or handling temperatures for oils and butters in real life. Thus, the stability of oils and butters containing rosemary extracts will actually be much more at normal handling temperatures.

Anti-microbial activity of rosemary extracts

Components of Rosemary extracts have been tested for anti-microbial properties by many researchers (10). At International Cosmetic Food Science Centre, we added 1250 ppm of Rosemary extracts and a chemical preservative composed of aliphatic paraben's in phenoxy-ethanol into an all purpose body lotion and conducted an anti-microbial test according to the method Ph. Eur. 4th Ed. (2002) 5.1.3. The four kinds of microbes chosen were, *Pseudomonas aeruginosa, Staphylococcus aureus, Can- dida albicans* and *Aspergillus niger*. The bacterial and fungal counts were monitored at start and after 2, 7, 14 and 28 days. In comparison to the efficacy of chemical preservative, Rosemary extract was very effective against microbes like *Pseudomonas aeruginosa* and *Staphylococcus aureus* while slightly less potent against *Candida albicans* and *Aspergillus niger*. The bacterial counts are shown in **Table 1**.

The numbers written in bold show the effect of Rosemary extracts while the ones in italics represent the effect of chemical preservative. The data indicate that use of rosemary extracts as anti-microbial agents enables a cosmetic formulator to reduce the dosage of synthetic preservatives.

Conclusion

The flooding of the skincare market with synthetics and chemicals can be controlled by using purely natural components. Use of internally stabilised lipids and Rosemary extracts has a number of additional benefits for formulators such as:

- Prolonged shelf-life of the cosmetic products they are used in.
- Stronger antioxidant properties compared to natural tocopherols.
- Strong antimicrobial properties which can reduce the amount of chemical preservatives in the final formulation of the skincare product.
- Strong anti-inflammatory and anti-aging properties.
- No need to add antioxidants in the formulation of the cosmetic product.
- Adds a more »natural« label to the product.

Thus, instead of adding synthetic antioxidants and preservatives into skincare formulations, use of internally stabilised vegetable oils and butters and naturally derived Rosemary extracts should be prescribed.

Literature

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Microbes	Initial count	After 2 days	After 7 days	After 14 days	After 28 days
Pseudomonas aeruginosa	6.3 x 10^5	**< 1 x 10^1** *190 x 10^1*	**< 1 x 10^1** *< 1 x 10^1*	**< 1 x 10^1** *< 1 x 10^1*	**< 1 x 10^1** *< 1 x 10^1*
Staphylococcus aureus	4.2 x 10^6	**< 1 x 10^1** *< 1 x 10^1*	**< 1 x 10^1** *< 1 x 10^1*	**< 1 x 10^1** *< 1 x 10^1*	**< 1 x 10^1** *< 1 x 10^1*
Candida albicans	4.8 x 10^6	150 x 10^3 *< 1 x 10^1*	320 x10^3 *< 1 x 10^1*	600 x 10^1 *< 1 x 10^1*	740 x 10^1 *< 1 x 10^1*
Aspergillus niger	1.4 x 10^5	64 x 10^1 *< 1 x 10^1*	80 x 10^1 *< 1 x 10^1*	27 x 10^2 *< 1 x 10^1*	38 x 10^2 *< 1 x 10^1*

Table 1 Anti-microbial effect of Rosemary extracts

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