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Enhancing the Stability of Natural Oils and Butters with Rosemary Extracts

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Key words

natural oils, butters, rosemary extracts, oxidative stability, antimicrobial activity, induction period

Abstract

Use of rosemary extracts to provide oxidative stability to various natural oils and exotic butters offers a way for formulators to reduce the use of synthetics and chemicals in skin care products.

Application of various oils and other natural materials for skin care or religious purposes is an ancient practice. Today the consumer market is flooded with innumerable skin care products. But whatever the type of product or branding, the presence of a lipoid material ties the modern day formulations to the ones of the ancient times.

Both natural oils and exotic butters are widely used in cosmetic products and nutraceuticals.[1] Evening primrose oil (*Oenothera biennis*) and borage oil (*Borago officinalis*) are very common natural oils, used primarily because of their high content of gamma linolenic acid, approximating 9-11% and 18-23%, respectively. Oils such as camelina oil (*Camelina sativa*), blackcurrant seed oil (*Ribes nigrum*) and flax seed oil (*Linum usitatissimum*) have cosmetic applications because they contain a high amount of polyunsaturated fatty acids.

Usually obtained from tropical jungle crops, exotic butters like shea (*Butyrospermum parkii*), mango (*Mangifera indica*) and sal (*Shorea robusta*) are among the exotic butters commonly used for skin care products. They are rich in symmetrical monounsaturated triglycerides that 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 and triterpines.[2]

Application of natural oils and butters in various cosmetic formulations is a great challenge in combating oxidation. This paper describes in detail how to avoid oxidation through natural processes, thus avoiding chemical additives.

Oxidation of Oils and Fats

The oil or fat content of a cosmetic product can vary from 2% to 15% in the case of body lotions and creams, while it can be as high as 100% in 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 and unpleasant tastes, and might lead to color change or increases in viscosity, specific gravity and solubility.

The mechanism of autoxidation has been postulated by many authors.[3-5] Autoxidation is a natural free radical process between molecular oxygen and the unsaturated fatty acids of an oil. This process leads to the formation of short-lived hydroperoxides (primary oxidation products). The hydroproxides readily break down to form alcohols, aldehydes, ketones and other hydrocarbons. These secondary oxidation products impart rancid odor and taste.[6] One way of preventing autoxidation is the 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, that does not contain some added preservatives. The antioxidants used are mostly synthetic, namely butylated hydroxytoluene (BHT), butylated hydroxyanisole (BHA), ascorbyl palmitate and tertiary butylhydroxyquinone (TBHQ). But consumer awareness of the possible toxic side effects of synthetic antioxidants and consumer preference for natural additives has led to more

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detailed investigations and applications of natural herb extracts as antioxidants.

In this study, the antioxidative effects of rosemary extracts were investigated in various oils and exotic butters. The oils tested were borage, flax seed, camelina, evening primrose and blackcurrant seed oil. The tested exotic butters were mango butter and shea butter.

Rosmarinus officinalis is a perennial herb of the *Labiatae* family. It has been used for seasoning, healing and various religious and medicinal rituals for thousands of years. Modern day technology has refined this tradition by scientifically extracting, identifying and applying the active ingredients of rosemary in various food and cosmetic products. Using supercritical CO_2 and other solvents like ethanol, the components of rosemary have been extracted and studied. The composition of rosemary extract is quite complex, consisting of a mixture of phenolic acids and diterpenes.[7]

The main antioxidative effect of rosemary extracts comes from three phenolic compounds: carnosic acid, carnosol and rosmarinic acid. More than 90% of the antioxidant activity is from carnosic acid and carnosol.[8] Flavonoids, particularly flavones, have also been identified in rosemary extracts. Rosemary extracts have also been reported to have antimicrobial, antiviral, antimutagenic and anticarcenogenic activity.[9]

Methods and Material

We used the oil stability index (OSI) as a tool to judge oxidation stability. We measured the OSI instrumentally[a], using the Rancimat principle that there is an increase of electrical conductivity because of the volatile carboxylic acids generated in the oxidizing 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 inflow was maintained at 18 lit/hr and the sample size was 3.5±0.05 g.

The fatty acid composition analysis was based primarily on IUPAC procedures 2.301 and 2.303. Each oil sample was saponified with potassium hydroxide in methanol, then esterified with boron trifluoride in methanol. The fatty acid methyl esters (FAMEs) in hexane are separated in a CP Sil 88 column (i.d.= 0.25 mm, d_f= 0.2 µm, 50 m in length), with an initial column temperature of 100°C to 225°C, 38 min, an injector temperature of 50°C (with a rapid temperature ramp to 250°C, 12 sec) and an detector temperature of 250°C.

The oils and butters and rosemary extracts were obtained from commercial suppliers.

The mango butter and shea butter were melted at a temperature higher than the corresponding melting point by about 10°C to ensure complete melting while the other oils, namely, camelina, flax, blackcurrant, evening primrose and borage, being liquid at room temperature were not heated. Rosemary extracts (1000±10 ppm) were added into each sample and stirred for 5 minutes at room temperature by a magnetic stirrer and then subjected to Rancimat analysis at temperatures different for different oils.

Results and Discussion

Fatty acids: The major fatty acids of the oils and butters used in this study are shown in Table 1.

Induction period: Classical autoxidation theory postulates three phases in the process.

- Initiation. In this first step, 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.
- Propagation. In the second step, 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.

[a] *Rancimat 679, Metrohm Ltd, Switzerland*

Table 1. Fatty acid composition (%) in selected oils and fats

Oil	C 16:0	C 18:0	C 18:1	C 18:2 n6	C 18:3 n3	C 18:3 GLA	C 20:0	C 20:1
Borage oil	11.2	4.1	17.2	36.5	0.2	20.3	0.6	4.3
Flax seed oil	5.5	3.5	19.1	15.3	56.6	-	0.4	0.1
Evening primrose oil	6.1	1.9	6.7	74.5	0.2	9.7	0.3	0.2
Blackcurrant oil	6.2	1.9	16.1	47.6	13.0	11.2	0.3	1.1
Camelina oil	5.3	2.9	18.7	16.0	38.8	-	1.1	11.5
Shea butter	4.9	41.9	45.3	5.5	0.1	-	1.5	0.3
Mango butter	7.9	38.5	44.7	4.3	0.5	-	2.4	0.2

- Termination. The third step involves the recombination of the various species of free radicals, resulting in 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 (IP). The longer the IP, the greater the oxidative stability of the oil.

IP correlates closely with the onset of rapid absorption and notable deterioration of flavor. This (IP) can thus be measured most directly by determining absorption of oxygen as a function of time.

The Rancimat values or IP, in hours, for different oils were grouped together and plotted as bar diagrams for comparison vis-à-vis the control sample containing no rosemary extracts. There were two groups: oils rich in polyunsaturated fatty acids are shown in Figure 1 (evening primrose), Figure 2 (blackcurrant and flax seed) and Figure 3 (borage and camelina). Exotic butters are shown in Figure 4 (shea and mango).

Oils rich in polyunsaturated fatty acids: Presence of high amounts of unsaturated fatty acids in oils not only makes them important for various applications but also extremely sensitive to oxidation. 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 in Figure 1.

From Figure 1, we see a steady and progressive increase of oxidative stability of evening primrose oil with increasing dosage of rosemary extracts. The IP of evening primrose oil increases almost linearly with increasing dosage of rosemary extracts. As the dosage increased from 270 ppm to 977 ppm, the IP 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 from 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 on blackcurrant seed oil and flax seed oil were observed from IPs at 80°C (Figure 2).

Similar to evening primrose oil, blackcurrant oil and flax seed oil also show improvement of oxidation stability on addition of rosemary extracts. IP of blackcurrant oil is increased to 38.5 hrs from 35.8 hrs while for flax seed oil, one of the most important vegetable sources of omega-3 linolenic acid, the 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 increases of oxidative stability due to addition of rosemary extracts (Figure 3). For borage oil, the IP is raised by about 25% while camelina oil shows a 33% rise in IP.

Exotic butters: The addition of rosemary extracts increased the oxidative stability of the tested exotic butters. The extent of increase is different in different butters, as illustrated with shea and mango butters in Figure 4.

Mango butter containing rosemary extract has an IP of 16.8 hrs (versus 11.6 hrs for the control) while shea butter

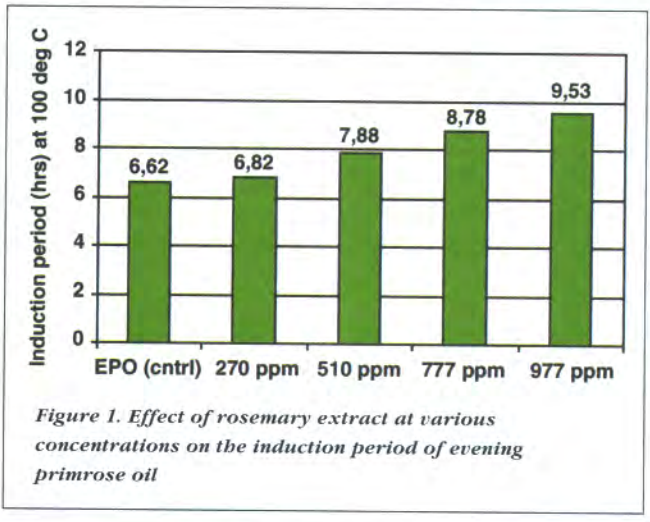

Figure 1. Effect of rosemary extract at various concentrations on the induction period of evening primrose oil

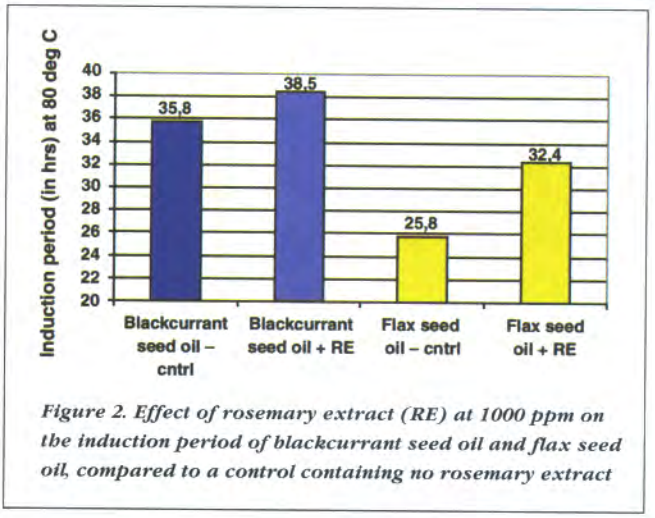

Figure 2. Effect of rosemary extract (RE) at 1000 ppm on the induction period of blackcurrant seed oil and flax seed oil, compared to a control containing no rosemary extract

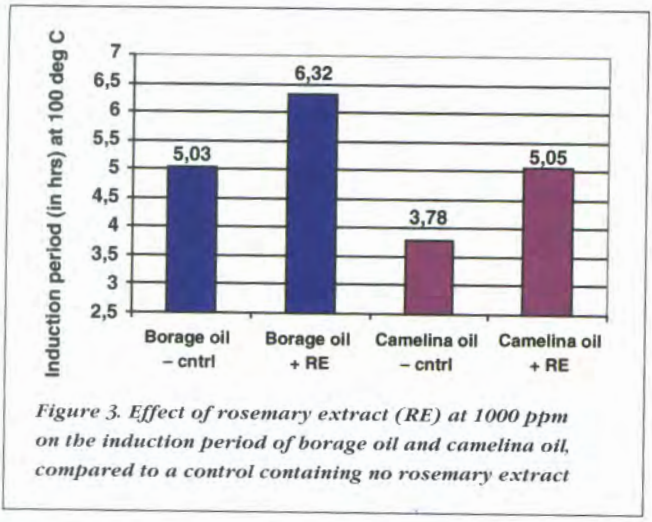

Figure 3. Effect of rosemary extract (RE) at 1000 ppm on the induction period of borage oil and camelina oil, compared to a control containing no rosemary extract

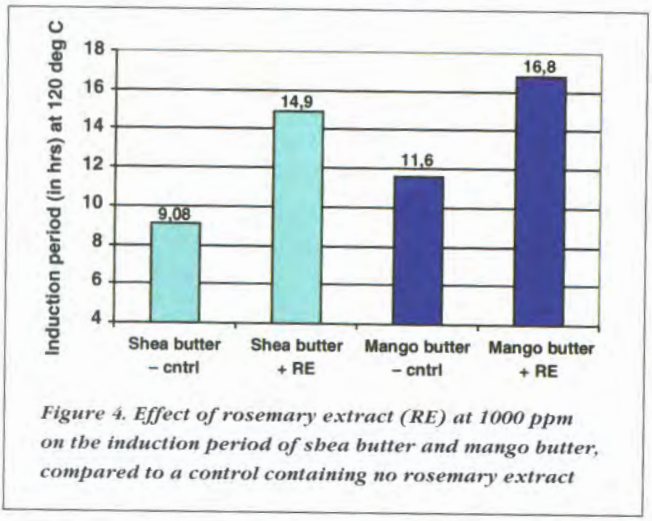

Figure 4. Effect of rosemary extract (RE) at 1000 ppm on the induction period of shea butter and mango butter, compared to a control containing no rosemary extract

has of IP of 14.9 hrs (versus 9.08 hrs for the control). Thus, addition of 1000 ppm of rosemary extracts gives mango butter a protection factor of 1.45 and shea butter a protection factor of 1.64.

From all the IP data obtained by Rancimat tests, we see a marked 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 interrupt the propagation step. In turn they form antioxidant radicals of very low activity inactivating any further reaction with lipids. It has been shown[10] 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 than most natural and synthetic antioxidants.

The presence of an antioxidant in an oil or fat cannot prolong the oxidative stability forever. Under strong oxidizing conditions, the antioxidants are soon used up and the gradual lowering of 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 better at normal handling temperatures.

Antimicrobial Activity of Rosemary Extracts

Components of rosemary extracts have been tested for antimicrobial properties by many researchers.[7] At International Food Science Centre, we added 1250 ppm of rosemary extracts and a chemical preservative composed of aliphatic parabens in phenoxyethanol into an all-purpose body lotion and conducted an antimicrobial test according to a standard method[b]. The four kinds of microbes chosen were *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Candida 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 the microbes *Pseudomonas aeruginosa* and *Staphylococcus aureus* while slightly less potent against *Candida albicans* and *Aspergillus niger*. The bacterial counts are shown in Table 2. Use of rosemary extracts may enable a cosmetic formulator to reduce the dosage of some synthetic preservatives in some formulations.

Conclusion and Future Perspectives

The flooding of the skin care market with synthetics and chemicals can be controlled by using purely natural components. Instead of adding synthetic antioxidants and preservatives into skin care formulations, use of natural oils and butters and naturally derived rosemary extracts should be prescribed. Use of rosemary extracts has a number of additional benefits for formulators such as:

[b] *Ph Eur 4th Ed (2002) 5.1.3.*

Table 2. Antimicrobial effect of rosemary extracts (red) and a chemical preservative (blue) in a body lotion

Count	*P. aeruginosa*	*S. aureus*	*C. albicans*	*A. niger*
Initial	6.3×10^5	4.2×10^6	4.8×10^6	1.4×10^5
After 2 days	$< 1 \times 10^1$	$< 1 \times 10^1$	150×10^3	64×10^1
	190×10^1	$< 1 \times 10^1$	$< 1 \times 10^1$	$< 1 \times 10^1$
After 7 days	$< 1 \times 10^1$	$< 1 \times 10^1$	320×10^3	80×10^1
	$< 1 \times 10^1$	$< 1 \times 10^1$	$< 1 \times 10^1$	$< 1 \times 10^1$
After 14 days	$< 1 \times 10^1$	$< 1 \times 10^1$	600×10^1	27×10^2
	$< 1 \times 10^1$	$< 1 \times 10^1$	$< 1 \times 10^1$	$< 1 \times 10^1$
After 28 days	$< 1 \times 10^1$	$< 1 \times 10^1$	740×10^1	38×10^2
	$< 1 \times 10^1$	$< 1 \times 10^1$	$< 1 \times 10^1$	$< 1 \times 10^1$

- 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 skin care 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.

Application of rosemary extracts often incorporates a distinctive flavor, characteristic of rosemary. This limits the use of rosemary extracts to a large extent in food and cosmetic products. International Cosmetic Science Centre has developed a process by which almost all the characteristic flavor and odor of rosemary can be removed from concentrated oil solutions of rosemary extracts.

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