Primer on Formulating NATURAL Products
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INTRODUCTION

One of the hottest areas in cosmetic formulations is the development of products that are considered “natural” by consumers, marketers, and regulators. Whether you are just starting out or are a seasoned formulator, getting a handle on the formulation of natural products is critical to your continued success. Traditional formulation techniques have focused on creating the best performing products at the lowest cost. Little regard has been given to the source of the starting raw materials. However, issues of sustainability, consumer desires and regulatory pressures have led to the need for the development of cosmetics using primarily plant-based, renewable resourced raw materials. This presents a special challenge to formulators as the starting materials often do not work as well as traditional synthetic ingredients.

In this short book, we have gathered experts to write chapters on the most important topics in the area of natural formulation. The book starts with a chapter on what it means to be a natural formulation and reviews some specific formulations that are touted as natural. The second chapter provides a thorough review of the various worldwide natural standards and gives direction on what type of ingredients can be included. The third and fourth chapters are written by naturals expert Art Georgalas and focus specifically on natural formulation types for skin care and hair care, respectively. The skin chapter focuses on creating natural emulsions, while hair topics include shampoos, conditioners, and styling aids.

The final two chapters explore the future challenges cosmetic chemists can expect to face as they continue to create natural formulations. The difficulty of proving the effectiveness and “naturalness” of ingredients is the subject of the fifth chapter. The sixth and final chapter details specific problems related to natural formulating and provides suggested solutions. This primer on natural formulations is meant as a starting point that will guide cosmetic chemists to a future world where petroleum derivatives are rarely used, and renewable, plant-based formulations are the norm.

We hope you find it useful.

All the best,

Perry Romanowski
Based on previously published studies and consumer articles, it appears that consumer interest in natural and organic products is growing. The question is: What does this mean? Are consumers actually interested in products that contain natural materials, or are they really interested in products that are safer and whose production or use have a minimal impact on the planet (i.e., they are renewable)? The key to meeting consumer demand is to understand what natural means in order to produce formulations that meet expectations.

Since the cosmetics and personal care industry is not regulated, various organizations have offered conflicting positions on standardized guidelines for natural and organic claims. To improve communication on this topic, it will therefore become important to dissociate claims regarding the naturalness of ingredients from the perception of safety.

Safety is inherent in the raw materials used for formulating, regardless of their origin and in the synergies among ingredients—for more than 50 years, the industry has worked hard to monitor the safety of products on the market, supported by the US Food and Drug Administration (FDA). And recently, more governmental agencies such as the FDA, the US Department of Agriculture (USDA) and the Council of Europe’s Committee of Experts on Cosmetic Products have taken a proactive role in sorting out the meanings of natural and organic for the cosmetics and personal care industry. Such organizations act as a clearer scientific focal point in deciding what ingredients are safe for use in cosmetic products. In addition, several organizations currently are monitoring the safety of cosmetics and personal care ingredients, such as the Cosmetic Ingredient Review (CIR) panel.
General Formula Standards

As noted, an ever-growing list of organizations with standardized guidelines exists that measures the naturalness of a product formula. The definition for *natural* in chemicals legislation was introduced in 1981, and in 2000, the Council of Europe’s Committee of Experts on Cosmetic Products issued guidelines for natural cosmetic products. Only as recently as 2008, however, did the USDA and the European Cosmetic Standards Working Group (COSMOS)\(^1\) provide additional guidance for formulating to meet natural claims. Nongovernmental, for-profit organizations offering organic and/or natural certification for cosmetic products include: Quality Assurance International,\(^2\) the National Science Foundation,\(^3\) ECOCERT,\(^4\) OASIS,\(^5\) Nature,\(^6\) the Soil Association, Guaranteed Organic Certification Agency,\(^7\) BDIH,\(^8\) the Natural Products Association,\(^9\) and Certech\(^10\)—to name a few. However, organic and natural certifications for cosmetics are not backed by specific legislation, such as in the foods industry.

**Formulas 1–5** are examples of natural products on the market, taken from sources of public domain and including estimates of the ingredient percentages used and/or their function in the formula, to provide readers with a starting point for their own formulation work. It is suggested that readers perform a patent search to ensure they are not infringing on any existing and protected technologies. In addition, two supplier-submitted examples of natural formulas are provided, for reader consideration.

### Formula 1. Burt’s Bees beeswax lip balm

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beeswax</td>
<td>qs</td>
</tr>
<tr>
<td>Coconut oil</td>
<td>2.05–5.0%</td>
</tr>
<tr>
<td>Sunflower oil</td>
<td>2.5–5.0</td>
</tr>
<tr>
<td>Tocopheryl acetate</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>Tocopherol (vitamin E)</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>Lanolin</td>
<td>0.5–1.0</td>
</tr>
<tr>
<td>Peppermint oil</td>
<td>&lt; 0.25</td>
</tr>
<tr>
<td>Comfrey root extract</td>
<td>&lt; 0.1</td>
</tr>
<tr>
<td>Rosemary extract</td>
<td>&lt; 0.1</td>
</tr>
</tbody>
</table>

### Formula 2. Tom’s of Maine lemongrass natural deodorant body bar

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soaps of coconut and palm</td>
<td>qs</td>
</tr>
<tr>
<td>Sage extract</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>Rosemary extract</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>Ascorbyl palmitate</td>
<td>&lt; 0.1%</td>
</tr>
<tr>
<td>Lemongrass oil</td>
<td>&lt; 0.25%</td>
</tr>
</tbody>
</table>

**Note:** These vegetable-based soaps include a blend of rosemary and vitamin C for preservation, and of sage and lemongrass for their reported natural odor-fighting properties.
Most natural products launched consist of at least 90% naturally derived materials and they omit certain ingredients construed as being unsafe, such as parabens. Cosmetic products meeting organic standards tend to follow USDA food standards, where no chemical fertilizers, herbicides, pesticides or other toxins were used to grow the non-hybridized plant sources from which the raw materials are derived. The most common denominators among formulas that meet claims for natural standards include:

- Ingredients based on environmentally conscious and ecologically sound practices that are socially responsible with regard to the use of resources, and that impart minimum human impact on the environment;
• Water is considered a basic ingredient; therefore, it is not included in the calculation for total percentage of natural or organic ingredients;
• At least 90% of the formula composition, sans water, is based on renewable feedstock and ingredients with neutral carbon footprints;
• Incidental ingredients such as preservatives, chelating agents and antioxidants do not have to be included in the calculation so long as they represent less than 1% of the non-water portion of the composition, and there are no renewable resource alternatives; and
• All raw materials used should represent the best approach to safe exposure to humans; safety measurements are based on scientific studies demonstrating their long-term safety to humans.

### Formula 4. All natural styling gel*

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dehydroxanthan gum (AMAZE XT polymer, Azko Nobel)</td>
<td>0.85% w/w</td>
</tr>
<tr>
<td>Deionized water (aqua)</td>
<td>50.00</td>
</tr>
<tr>
<td>Tapioca starch (Naviance Tapioca certified organic biopolymer, Azko Nobel)</td>
<td>2.50</td>
</tr>
<tr>
<td>Deionized water (aqua)</td>
<td>44.95</td>
</tr>
<tr>
<td>Glycerin (vegetable grade)</td>
<td>0.25</td>
</tr>
<tr>
<td>Sodium benzoate</td>
<td>1.00</td>
</tr>
<tr>
<td>Benzyl alcohol</td>
<td>0.25</td>
</tr>
<tr>
<td>Hydrolyzed wheat protein (and) hydrolyzed wheat starch (and) water (aqua)</td>
<td>0.20</td>
</tr>
<tr>
<td></td>
<td>100.00</td>
</tr>
</tbody>
</table>

**Procedure**: Without heat, slowly sift A into B with good agitation (700 rpm), until completely dispersed. Reduce mixing speed to 400 rpm and mix for 15 min to completely hydrate. In a separate mixing vessel, sift C into D with good agitation (~ 400 rpm) and mix until completely dispersed. Slowly add CD to AB. Continue mixing at ~ 400 rpm and heat to 80°C. Hold for 25 min. Cool to 45°C before adding E in order. Mix until homogenous. Fill containers. Viscosity: 15,000–20,000 cps; Brkfld Heliopath Spindle #T-C /10 rpm; pH 5.0–7.0

*Note: Formula provided courtesy of Akzo Nobel; naturally derived ingredients in this styling gel provide moderate stiffness with humidity resistance and a pleasant aesthetic feel. Tapioca starch offers texture and hold with excellent aesthetics while dehydroxanthan gum polymer yields rheology and high humidity hold.

In general, the key to formulating natural products is to choose safe and effective raw materials of as natural an origin as possible. Their
renewability also should be incorporated into the product development process, to result in the smallest possible negative footprint on the environment. However, for product developers to meet the specific requirements of a given standard, it is important to fully understand the requirements since they can vary as to how the percentage of natural ingredients is calculated, or the degree of modification allowed to a natural source material. This is important because some natural ingredients are either not functionally suitable to create good aesthetics, are not stable, or are not sufficiently pure—odorless and colorless.

**Formula 5. All natural sunscreen lotion***

<table>
<thead>
<tr>
<th>A. Deionized water (aqua)</th>
<th>qs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zinc oxide</td>
<td>10.00% w/w</td>
</tr>
<tr>
<td>B. Glycerin</td>
<td>2.50</td>
</tr>
<tr>
<td>Xantham gum</td>
<td>0.50</td>
</tr>
<tr>
<td>C. Cetearyl alcohol (and) coco glucoside</td>
<td>3.00</td>
</tr>
<tr>
<td>Sorbitan sesquioleate</td>
<td>0.75</td>
</tr>
<tr>
<td>White beeswax</td>
<td>1.50</td>
</tr>
<tr>
<td><em>Butyrospermum parkii</em> (shea butter)</td>
<td>1.50</td>
</tr>
<tr>
<td><em>Simmondsia chinensis</em> (jojoba) seed oil</td>
<td>1.00</td>
</tr>
<tr>
<td><em>Prunus amygdalus dulcis</em> (sweet almond)</td>
<td>0.50</td>
</tr>
<tr>
<td><em>Sesamum indicum</em> (sesame) oil</td>
<td>0.50</td>
</tr>
<tr>
<td>Tocopheryl acetate (vitamin E acetate)</td>
<td>0.50</td>
</tr>
<tr>
<td>Bisabolol nat.</td>
<td>0.20</td>
</tr>
</tbody>
</table>

**Procedure:** Combine A, mix well and heat to 75–80°C. Premix B and add to A at 75°C while homogenizing. Separately combine C, heat to 75°C and add C to AB at 75°C, homogenizing until batch is uniform. Transfer batch to sweep mixing and cool to 40°C. Add D in order and mix until room temperature. Homogenize at slow to medium speed till batch uniform, then stop.

*Note: Formula provided courtesy of BASF.

**Conclusions**

The continued market demand for natural products is growing, and while the definition of *natural* remains an ongoing discussion, there is a definite push toward eliminating classical, “chemical-sounding” ingredients, even if they are proven safe and have little or no impact on the planet. Since the concept of *natural* and how it is positioned in the marketplace is still a moving target with minimal legal standardization, it will take some time to provide formulators with a clear idea of how to find and utilize the right materials that support this market claim.
Current standards are dependent upon the marketing division within individual companies and their legal department. For now, it is best for formulators to work with their company’s legal, regulatory and marketing groups to agree on how natural will be defined and stay true to the course. Then it will be easier to work with raw material suppliers to document and match to these specification requirements.

Various organizations including those previously listed, whose Web sites may be found in the concluding references to this chapter, have developed a list of acceptable and unacceptable renewable ingredients that would meet their standards for natural and organic claims. Also, a number of raw material suppliers have published prototype formulations for use as starting points for natural product formulations.

The development of personal care products for this market requires clear communication regarding whether said products will be positioned as natural—meaning either containing natural ingredients or being safer for the environment; organic and thus meeting a set of specified standards; or renewable, referencing low impact on resources in the environment. In addition, such products should outline the source of feedstock from which their ingredients derived, as well as the renewability and greenness of the source; and safety assurance based on reliable, peer-reviewed science and scientific organizations.

The personal care industry must take a leadership role, as it has for the past 50 years with other issues, to control the misleading association of terms such as natural and organic with the consumer’s expectation of implied safety; the industry must continue in its defense of ingredients with established safety.

References
1. www.cosmos-standard.org
2. www.qai-inc.com
4. www.ecocert.com
5. www.oasisseal.org
6. www.nattrue.org
7. www.goca.ws/organic-certification
8. www.kontrollierte-naturkosmetik.de/e/bdih.htm
Every once in a while, readers ask how topics are selected for this column. This time, the idea came from an e-mail inquiring what COSMOS standards are. Previous columns have discussed Canadian Natural Health Products regulations but have steered clear of the natural and organic debate, although this author previously published an article that debates animal versus vegetable ingredients, in which he explains that a chemical is a chemical regardless of its origin; a molecule of glycerin is just that, whether from natural sources like animal or vegetable fat, or from petroleum or biodiesel sources.

COSMOS is the European Union’s (EU) newest effort to outline organic and natural standards, with draft guidelines published in November 2008. But how is it different than other standards? This calls for a review of the various natural and organic standards for the personal care industry and how they have evolved.

What is Natural?
According to the author, when he first began to learn during the Dark Ages, the elements of earth, air, fire and water were understood to be natural; thus everything made from them was considered natural. Later, industry expert Ken Klein stated that anything made from the first 92 elements of the periodic table are natural, and that no man-made elements should be used in products claiming to be natural; however, this philosophy did not seem a sufficient answer for what marketers where claiming.
An Internet investigation retrieved several meanings for the term *natural*, among which were: being present in or produced by nature; i.e., *a natural pearl*; being inherent or not acquired; not being produced or changed artificially; and not being altered, treated or disguised.

The US Food and Drug Administration (FDA) does not define natural in the Food, Drug and Cosmetic Act or any other FDA regulation; the closest definition for natural personal care products was established in Canada as a regulated category called Natural Health Products. This regulation, which went into effect on Jan. 1, 2004, defines natural health products (NHPs) as: vitamins and minerals, herbal remedies, homeopathic medicines, traditional medicine such as traditional Chinese medicine, probiotics, and other products like amino acids and essential fatty acids.

While these materials are found in nature, Canada took it a step further to describe acceptable substances as being synthetic duplicates of those materials listed above. Synthetic duplicates are substances that share identical chemical structures and pharmacological properties with their natural counterparts; an example of such is vitamin E and dl alpha-tocopherol.

A semi-synthetic substance may also be acceptable as an NHP, provided that it shares identical chemical structures and pharmacological properties with its natural counterpart. Semi-synthetic substances are produced by processes that chemically change a related starting material that has been extracted or isolated from a plant or a plant material, an alga, a fungus or a non-human animal material. An example of such is ginsenosides, which are produced from the starting compound betulafolienetriol.

In the end, whatever marketing deems natural is natural; the critical inference is that consumers believe products marketed as natural are safer than products that are not marketed as natural. This has given rise to an increase in use of the word *organic* within the cosmetic industry.

Organic

Recalling studies from his youth, the author notes that the term *organic* originally referred to the chemistry of the carbon atom. Then in 1973, an organization called the California Certified Organic Farmer was formed to promote organic farming in California, instilling in the
public a new sense of the word *organic*. This group became one of the first to certify products with an organic seal of approval on the label. In 1979, the state made the organic labeling of foods a law subject to their controls.

In 1980, the US Department of Agriculture (USDA) published its “Report and Recommendations on Organic Farming,” in which organic farming was described as a “production system that avoids or largely excludes the use of synthetically compounded fertilizers, pesticides, growth regulators and livestock feed additives. To the maximum extent feasible, organic farming systems rely upon crop rotations, crop residues, animal manures, legumes, green manures, off-farm organic wastes, mechanical cultivation, mineral-bearing rocks and aspects of biological pest control to maintain soil productivity and tilth, to supply plant nutrients and to control insects, weeds and other pests.”

Reasons for interest in this system included:
- Increased cost and uncertain availability of energy and chemicals;
- Increased resistance of weeds and insects to pesticides;
- Decline in soil productivity from erosion and accompanying loss of organic matter and plant nutrients;
- Pollution of surface waters with agricultural chemicals and sediment;
- Destruction of wildlife, bees and beneficial insects by pesticides;
- Hazards to human and animal health from pesticides and feed additives;
- Detrimental effects of agricultural chemicals on food quality;
- Depletion of finite reserves of concentrated plant nutrients (e.g., phosphate rock); and
- Decrease in numbers of farms, particularly family-type farms, and disappearance of localized and direct marketing systems.

By the late 1980s, a number of private and state-run certifying bodies were operating in the United States. Standards varied among these entities, causing trouble in commerce. Certifiers often refused to recognize products certified as organic by other agents, which was a problem particularly for organic livestock producers seeking feed, and
for processors trying to source ingredients. In addition, a number of well-publicized incidents of fraud began to undermine the credibility of the organic industry.

In an effort to curb these problems, the organic community pursued federal legislation. The result was the Organic Foods Production Act of 1990, which mandated the creation of the National Organic Program (NOP) and the passage of uniform organic standards. These standards were incorporated into NOP regulations. Implementation of the regulations began on April 21, 2001, and all organic certifiers, producers, processors and handlers were required to be in full compliance by Oct. 21, 2002.

Beyond federal legislation, the California Organic Products Act (COPA) was signed into law in 2003, and beginning Jan. 1, 2003, all products sold in California containing a total of less than 70% organic ingredients were no longer allowed to use the word organic on the front labeling panel. Later in 2003, the State Assembly repealed the non-food provision of the COPA but in the end, cosmetics remained a part of the Act.

With the growth of nationwide food stores based on certified organic foods, interest in the organic market has spread to cosmetics and other personal care products. From this interest, several groups have emerged with varying standards for organic certification; most use a seal that appears on product labels to indicate organic certification. Following are some of the major bodies, as well as their requirements. This is not a comprehensive list but it will provide an overview.

**National Organic Program (NOP, United States):** Within this program are four levels of organic claims for foods. The NOP defines the claims that can be used for agricultural products by their content, excluding water and salt.

**100% Organic:** For this claim, 100% of the ingredients in the product must be certified organic products and in this case, the USDA Organic seal may be used (see Figure 1).

**Organic:** To make this claim, 95% of the materials in the product...
must be certified organic products; the same USDA Organic seal may be used in this instance.

*Made with organic ingredients:* For this label claim, 70% to 94.99% of the product’s ingredients must be certified organic; in this case, use of the USDA Organic seal is not permitted.

*Contains organic:* This label claim requires less than 70% of certified organic ingredients in a product and also cannot bear the USDA Organic seal.

**Natural Products Association (NPA, United States):** This organization was founded in 1936 and was principally concerned with dietary supplements. The group represents more than 10,000 retailers, manufacturers, wholesalers and distributors of natural products, including foods, dietary supplements, and health and beauty aids. On May 1, 2008, the group issued its certification program for personal care products. In order to display the NPA seal (see Figure 2), a product must meet the following requirements:

- Contain at least 95% truly natural ingredients or ingredients that are derived from natural sources;
- Contain no ingredients linked with potentially suspected human health risks;
- Not be processed in ways that significantly or adversely alter the purity of its natural ingredients;
- Include ingredients derived from a purposeful, renewable/plentiful source found in nature (flora, fauna, mineral);
- Be minimally processed and avoid the use of synthetic or harsh chemicals so as not to dilute the material’s purity; and
- Should contain non-natural ingredients only where viable natural alternative ingredients are unavailable, and only when they pose absolutely no potentially suspected human health risks.

The Natural Products Association also has published a list including 839 ingredients that it considers meets these requirements.
Cosmetics Organic and Natural Standard (COSMOS, EU): As noted above, COSMOS is one of the EU’s newest efforts, with its draft published in November 2008. This standard was developed from collaborations between working groups including: the Instituto per la Certificazione Etica e Ambientale (ICEA in Italy); the Federation of German Industries and Trading Firms for Pharmaceuticals, Health Care Goods, Dietary Supplements and Personal Hygiene products (BDIH in Germany); Bioforum in Belgium; the French Professional Association of the Ecological and Organic Cosmetics, and a French certification organization (Cosmebio/Ecocert in France); and an environmental charity promoting sustainable, organic farming and championing human health (The Soil Association in the UK). The COSMOS draft is available at www.cosmos-standard.org.

These standards describe five categories of ingredients: water, minerals, physically processed agro-ingredients, chemically processed agro-ingredients and synthetic materials. The draft details what materials are and are not allowed. It is interesting to note the chemical reactions that are and are not allowed (see COSMOS Chemical Reactions).

Under Appendix II of the COSMOS standard, the following synthetic ingredients are allowed: benzoic acid, benzyl alcohol, dehydroacetic acid, denatonium benzoate, heliotropine, salicylic acid, sorbic acid and tetrasodium glutamate diacetate. The second part of Appendix II lists the mineral origin products allowed—which contradicts the initial five categories of organic ingredients listed since “mineral” is included one of the organic ingredient categories.

California Organic Program (United States): Products sold in California must comply with the 2003 COPA Act to be labeled organic. These products also must be at least 70% organic, not including water and salt content. Like the USDA program, this program attempts to apply a food law to cosmetics. All organic ingredients used in organic products must be certified by one of the organizations listed by the USDA. There are additional registration fees and other labeling requirements.

Organic and Sustainable Industry Standards (OASIS, United States): OASIS was developed and is observed by major cosmetic companies in the United States such as L’Oréal and Estée Lauder. This standard certifies products at two levels—organic or made with organic. The made
COSMOS Chemical Reactions

Allowed physical processes:
- Extractions must use natural materials with any form of water or with a third solvent of plant origin such as ethyl alcohol, glycerin, vegetable oils and CO₂ absorption (on an inert support that conforms to these standards);
- Bleaching or deodorization (on an inert support conforming to these standards);
- Grinding, centrifuging (solid/liquid separation, spin-drying);
- Settling, decanting, desiccation or drying (progressive or not by evaporation/natural under sun);
- Deterpenation (if fractionated distillation with steam);
- Distillation, expression or extraction (steam);
- Filtration and purification (ultra filtration, dialysis, crystallization and ion exchange);
- Lyophilization, blending, percolation, cold pressure and hot pressure (depending on the fluidity of the fatty acids to be extracted);
- Sterilization with thermal treatments (according to a temperature respectful of the active substances); and
- Sifting, maceration and ultrasound

Allowed chemical processes:
- Alkylation, amidation, calcination of plant residues and carbonization (resins, fatty organic oils);
- Condensation/addition, esterification, etherification and fermentation (natural/biotechnological);
- Hydration, hydrogenation, hydrolysis and neutralization (to obtain Na, Ca, Mg and K salts);
- Oxidation/reduction processes for the manufacture of amphoterics; and
- Saponification, sulphation and roasting

Unallowed processes:
Any other processes that are not listed above are not allowed, including but not limited to:
- Bleaching or deodorization (on a support of animal origin);
- Use of enzymes derived from GMOs;
- Deterpenation (other than with beam);
- Ethoxylation, irradiation and sulphonation (as the main reaction);
with organic designation requires 70% minimum organic content with additional criteria for the remaining 30% of ingredients. The organic label claim will require a minimum of 85% organic content until January 2010, at which time it will increase to a requirement of 90% minimum organic content; the minimum requirement will increase a third time to 95% by 2012. Products that cannot achieve a 95% organic level, such as soap, must use the made with organic claim.

This interval approach takes into consideration the fact that at least two years are necessary for surfactant and emulsifier manufacturers to put enough products into the commercial stream to supply the industry with organic versions of functional ingredients. Since one of the goals of OASIS is to promote the development of more raw materials developed from organic starting materials, this approach works with chemical manufacturers to achieve these goals.¹¹

Whole Foods—Premium Body Care Seal (United States): One of the major retail outlets for organic products is the Whole Foods supermarket chain. This group has established its own rules and symbol. As of press time, the author has not been able to obtain the rules or the symbol. The group lists more than 250 ingredients that are not allowed, and also does not allow animal testing or organic UV filters. The group is aligned with the Environmental Working Group (EWG).

Organic Consumers Association (United States): This final group was established in 1998 in opposition to the USDA’s NOP program, and deals primarily with the food area. It has been involved in litigation with other standards.¹²
Comments
What chaos. Why are there so many different organizations, standards, symbols—and now, lawsuits? There is only one answer: marketing. One may question whether the companies selling cosmetics stamped with these symbols care about anything more than selling products. The underlying message is that consumers have been misled to believe that these products are safer than non-natural or non-organic cosmetics. These organizations’ definitions are contradictory and in some ways, amusing. One set of rules states that water found in the *Aloe barbadensis* leaf is organic while water from the faucet is not. Water is water is water. Also, natural minerals are allowed as colorants but they cannot be processed; as a minor point, this means that with the exception of mica, none of these natural minerals would be permitted in cosmetics. Natural iron oxides, for example, would be in violation of FDA, EU and Japanese standards since ground iron oxide ores have enough lead, mercury, arsenic, cadmium, etc., in them to keep Proposition 65 lawyers in California busy filing lawsuits forever.

Natural does not mean safe. In fact, the NPA’s list of permitted “safe ingredients” includes 15 of the EU’s 26 listed fragrance allergens. Perhaps natural allergens are better, then? And while one firm stands behind the EWG and proclaims that synthetic UV filters are dangerous, only permitting ZnO and TiO$_2$, the International Agency for Research on Cancer has in the meantime declared TiO$_2$ to be a known human carcinogen; plus, synthetic ZnO is the only ZnO used since its natural ore only exists with lead.

How far can this go? Do natural or organic cosmetics impart real benefits or are they just another marketing fad? As the economy in the United States declines, it appears that consumers are still spending money for organic foods but are foregoing higher priced organic personal care products.

This column is titled “Caveat Emptor,” which means “let the buyer beware.” This column also calls to mind a quote by David Hannum, among others, that states: “There’s a sucker born every minute.” In this author’s opinion, that is what keeps these products on the store shelf.
References

4. Ibid Ref 3, pp 13
5. Ibid Ref 3, pp 16–17
11. Ibid Ref 9
When formulating skin care with natural ingredients the first question to ask is: With which definition of natural will the product conform? The definition might be significantly different for the general public than for consumers following lifestyles of health and sustainability (LOHAS) philosophies. However, one may wonder what even these purist consumers know about the myriad of natural and organic certifications out there. This author would venture that most consumers’ identification for natural products would be analogous to Chief Justice Stewart’s definition of obscenity—i.e., “I know it when I see it.”

While market research firms specialized in this market have undoubtedly conducted surveys to understand what consumers view as natural, the current picture is likely quite variable. When, if ever, consumers come to a general consensus and accept one or more of the various competing natural and organic standards, formulators can follow those standards; but right now there are simply too many.

**Approaches to Natural**

Should the formulator choose ingredients from the multitude given the Ecocert imprimatur, or choose those on the Natural Products Association’s list of 800+ acceptable materials? Or should the formulator instead avoid ingredients found on the Whole Foods list of nearly 400 unacceptable ingredients? Then there are the criteria set forth by NaTrue or the National Sanitation Foundation/American National Standards Institute (NSF/ANSI); the European cosmetics standards working group, also known as the COSMOS consortium; as well as the Organic and Sustainable Industry Standards (OASIS) industry group in the United States. Formulators may just want to follow...
the guidance of renowned expert Ken Klein and use only materials composed of the first 92 naturally occurring elements. Again, who defines what’s natural?

Further, official governing bodies provide little more guidance. For example, the US Food and Drug Administration (FDA) gives no formal definition for natural except to state that natural ingredients come from natural sources. Regarding foods, the “FDA has not developed a definition for use of the term ‘natural’ or its derivatives,” but a product is considered a natural food when it contains no artificial or synthetic ingredients and is only minimally processed according to the 2005 food labeling guidelines.

Verbiage in the European Union’s (EU) REACH regulation states, “A naturally occurring substance is such [that is] unprocessed, or processed by manual, mechanical gravitational means; by dissolution in water; by flotation; by extraction with water; by steam distillation; or by heating solely to remove water, or which is extracted from air by any means.”

The International Organization for Standardization (ISO) has issued vocabulary for natural aromatic substances in ISO 9235:1997, developed by the essential oil technical committee (TC) 54, and is currently working on ISO/NP 16128, “Cosmetics—Technical definitions and criteria for ‘natural’ and ‘organic’ ingredients and products,” which is at the approved new project stage for ISO TC 217: Cosmetics. Perhaps this is what Julie Tyrrell of NaTrue is referring to on the group’s website when she says, “The criteria for ‘natural’ claims should be finalized in the second half of 2011 and become operational from 2012 based on legislation in EU Parliament Article 20 that restricts false claims for cosmetics.”

At the Bench: Lipids and Proteins

When formulators finally get to the bench to begin building natural skin care products, they can begin with the basic ingredients for emulsions: emollients, emulsifiers, humectants, thickeners, preservatives and other stabilizers, colors and fragrance. By focusing on these key components, one can identify candidates from their compendium of natural ingredients. Skin care emollients are generally easy since there are many to choose from, although they consist primarily of the natural
triglycerides—i.e., fatty oils and butters. Add to this jojoba oil, strictly speaking a liquid wax ester, and squalene, a triterpene precursor of the sterol backbone distilled from olive oil as the major unsaponifiable liquid lipid and the basic ingredient list is all but exhausted.

Oxidatively unstable squalene becomes the elegant branched chain natural hydrocarbon squalane upon hydrogenation, a chemical process that is allowed in many certification schemes. Of course the question then arises: Is this truly natural? Other, lighter hydrocarbon components can be extracted by fractional distillation from natural oils, allowing for the adjustment of feel with mixtures of these oils, butters and other lipids. In general, lower molecular weight and less polar oils with branching and unsaturation give a lighter feel. Unsaturated oils may be challenged by oxidation leading to potential rancidity.

Considering the emulsification mechanism itself, the formulator might ask: What does nature do? How are stable oil and water systems established in nature? Nature works at a molecular level to produce the results observed macroscopically. Tiny, subcellular nanofactories churn chemicals out one molecule at a time that are then harvested by industry in bushel baskets and stainless steel vats. For instance, the olive oil that consumers serve at the dinner table begins as single triglycerides produced by the olive tree’s lipid synthesis pathway.

The stabilization of these two-phase systems in nature usually involves complex combinations of lipids and proteins. Some commercially available natural emulsions include oleosomes—lipid bodies in oil seeds such as safflower that stabilize vegetable oil droplets for seed storage by coating them in oleosin protein. Mammalian milk is also stabilized by proteins, among which are caseins—one of the major milk protein groups present as micelles that disperse milk fat.

In addition, plant latex, found in more than 20,000 species including guayule, milkweed, poinsettia and many Euphorbiaceae and other botanical families, is stabilized in laticiferous (milk-forming) systems with the help of proteins plus polar lecithin lipids and other components. Studies of the Hevea species, the chief rubber-producing plant, show an adsorbed sheath of protein on the surface, stabilizing the particles of isoprenoid oils that comprise rubber’s source hydrocarbons. This protein gives the oil droplets electrophoretic mobility, i.e. a zeta potential, and stabilizes them via surface electrostatic charges. In fact, many proteins are known
to have surfactant properties based on the relative hydrophobicity of their amino acid side chains and ionizable groups, a major factor in governing their tertiary structure. Even relatively small hydrolyzed proteins have surface activity that can contribute to emulsion stabilization. Formulators should look both inside and outside of the cosmetic buyer’s guide for proteins to assist in the natural stabilization of dispersed systems.⁹

If one allows for simple kitchen chemistry processes such as saponification in the development of natural products, a range of soap surfactants based on vegetable oils are also available, most commonly coconut, palm kernel and soy. Use of the strongly alkaline amino acid arginine in the free base form can be an unusual natural alternative to simple mineral alkali or ammonia for neutralization, replacing the much maligned triethanolamine (TEA).¹⁰ In addition, waxes such as beeswax and candellila can supply naturally occurring free fatty acids for soap formation since both have acid values near 20; in fact, one company reports that a certified organic emulsion can be prepared using the US Department of Agriculture’s (USDA) NOP beeswax.¹¹

Other natural amphiphiles that can be combined or used individually include the phospholipid lecithins and lanolin, the wool wax-based mixture of sterol esters, plant sterols and saponins, as well as a range of commercial plant sterol and triterpenoid glycosides extracted from soapwort and agave.

Formulators should note that lecithins can have a varied hydrophilic-lipophilic balance (HLB), depending on the degree of hydrolysis and extraction methods, which can be useful for both o/w and w/o emulsions. Unmodified sterols are exclusively w/o stabilizers whereas the saponin glycosides, as their name implies, act like soaps and are used more for foam generation.

Carbohydrates

Natural thickeners and stabilizers from the carbohydrate group of polymers include many of the plant gums of microbial, algal and vascular plant origin. These gums modify the texture and flow properties of emulsions and add to their physical stability. Xanthan gum is a mainstay of food emulsion preparation and is one of the few ingredients named in the USDA’s list of allowed additives to organic-certified processed foods. It imparts the shear thinning rheology with significant yield
value necessary to give creams and lotions shelf stability with desired feel at acceptably low use levels of a few tenths percent.

Additional vegetable gums having varying degrees of emulsification, stabilization and viscosity control include tragacanth, scleroglucans, guar, locust bean, carageenan and the alginates, many of which demonstrate synergy, suggesting trials of varying mixtures. Simple insoluble cellulose itself also has been used in the form of citrus fibers and microcrystalline cellulose. Another soluble complex carbohydrate for dispersion enhancement and reduced, more homogeneous emulsion particle sizes is galactoarabinan from the Larch tree. Further, naturals of the mineral variety including swellable clays such as bentonite are useful for their water-structuring ability, forming a hydrated “house of cards” on high shear dispersion. They are also especially effective in combination with natural gums.

Emulsion Construction
The three primary plant metabolite groups described, i.e. lipids, proteins and carbohydrates, provide the scaffold and building blocks for emulsion construction. Some of the starting materials for these polymers also function as humectants in finished products, notably glycerol and amino acids such as pyrrolidone carboxylic acid (PCA) and sugar alcohols such as sorbitol. From the range of secondary plant metabolites identified, mostly polyphenols and terpenoids, the ancillary components of emulsions—colors, fragrances and preservatives as well as some botanical actives, are sourced; botanical actives will be addressed in a future column.

When nature-derived materials are difficult to obtain, nature-identical compounds can be synthesized that function virtually the same—as long as they are not chiral compounds and they are sufficiently purified. The NaTrue organization, for one, goes to great lengths to identify the nature-equivalent preservatives they allow, including such organic acids as sorbic, benzoic, salicylic and dehydroacetic and their salts as well as benzyl alcohol.

Allowed organic cosmetic colorants, as listed in the US Code of Federal Regulations (CFR) 21, part 73, include annatto orange-red and beta-carotene, both yellow-orange, oil-soluble carotenoids, as well as carmine, the red polyphenol pigment derived from carminic acid
from the cochineal bug. It should be noted that many nature-derived food colorants such as beet extract are only specifically approved for foods, not cosmetics.

To fragrance the emulsion, numerous natural flower and fruit scents are available. From this author’s limited experience in fragrance, chamomile essential oil is suggested as a good starting scent since it works at low levels to mask many base odors with a pleasant and persistent floral note. Natural fragrancing is an art that requires an expert to achieve the right result but suffice it to say it is quite possible to naturally fragrance most products the formulator may envision.

Conclusion

Overall, formulators may limit their range by choosing to go truly natural; however, with some background information and a good deal of experimentation, a variety of effective and aesthetic skin care emulsions can be formulated. When the ingredient range is expanded to naturally derived and nature-identical compounds, the formulator’s palette expands to an even greater variety. In either case, hopefully these strictures placed on formulators will engender innovation rather than stifle creativity in the development of natural products with greater benefits for the end user.

Lab Practical: Using Naturals

- Natural materials have more microbes, and microbial limits for food products are sometimes higher than cosmetics. Be sure to check and control the microbe content.
- Natural materials have a wider variability. Specifications should be set and supplies should be screened critically.
- Naturals have more natural color and odor. This should be considered when setting formulated product specifications and choosing fragrances and masking agents.
- Naturals can be more heat/processing sensitive. Formulators should be aware of how heat, shear and order of addition affect the final result and formula reproducibility.
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Today, hair care formulators aiming to formulate for the natural market are in a quandary as the performance of modern products is driven more and more by the use of innovative new synthetic materials. The bench chemist witnesses the weekly arrival of new iterations as manufacturers graft one functionality onto another to try to outdo the competition. Cosmetic chemists cannot seem to get enough of different silicone copolymers, acrylate cross polymers, quaterniums, polyquaterniums and syndets—and whatever hybrids the organic chemists can create—since high performance is generally imagined to require high-tech ingredients.

However, some formulators march to the beat of a different drummer, guided by a more natural rhythm, so their ingredient choices may be more restricted. Of the raw materials essential for advanced hair formulas, the two major types that are problematic for natural recipes are polymers and surfactants. This is not because they do not exist in nature but because formulators constrain themselves within the boundaries of what is viewed as acceptable in formulas labeled as natural. Regardless of which certifying organization is used to guide formulating choices, performance should not be sacrificed for a natural certification. This dictum from marketing and management holds sway in most companies unless a product line raison d’être overrides it.

Naturals Guidance
While the industry is not yet at the point where one certifying body has come to the forefront, there seems to be a consensus of do’s and don’ts among them. Lists of acceptable and unacceptable materials are generated based on safety and environmental concerns. In addition,
certain chemical and physical processes may be given the imprimatur of that organization in order to display their logo. Under all natural and organic cosmetic standards, the agricultural practices of irradiation for sterilization and the use of sewage sludge fertilizer, or employment of genetically modified organisms, are as universally forbidden as they are with the original farm products. Further, some chemical processes including ethoxylation are universally restricted, while some processes such as hydrogenation and esterification are generally accepted.

**Ecocert:** Many formulators and raw material suppliers have jumped on the Ecocert bandwagon. This may be because Ecocert led the way initially, thus the volume of materials available to formulators under this certification standard is significantly larger than others. But even when Ecocert-approved cosmetics reach store shelves, many consumers, including those familiar with natural and organic certifications, will scratch their heads and wonder how many of the “chemical-sounding” ingredients listed on the label are natural. To paraphrase another cliché or platitude, natural is in the mind of the beholder. It’s all about perception; consumers are put off by chemical names, and INCI nomenclature does not always help in this respect—in some cases, baffling even chemists about what chemicals are actually contained in the product.

**COSMOS:** The Cosmetics Organic Standard (COSMOS) in Europe arose as a consensus among six national organizations, including Ecocert. This group published a final rule in January 2010 that accommodates different levels of ecotoxicology for different degrees of biodegradability—a fairly rational way to measure relative environmental risk. The greater the aquatic toxicity, up to a maximum, the more completely the compound must biodegrade. Conversely, the lower the toxicity, the less biodegradable the compound must be, within limits. Restricted compounds that persist in the environment, that are not biodegradable, or that are bioaccumulative, i.e., retained in an organism’s tissues, are prohibited.

**NaTrue:** NaTrue, another European natural products certifier, recently announced it will form a harmonized natural standard in collaboration with NSF International, brokered by the Quality Assurance International (QAI) organization. QAI has taken a lead in promoting the NSF/ANSI 305 standards that it administers and is proactive in providing education for these standards. NaTrue’s standard states that
any detergent surfactants used must be completely biodegradable in accordance with the European Commission’s Regulation on Detergents; however, other materials were not specifically addressed as recently as early February 2011.4

**USDA:** In the United States, natural product guidance was recently complicated by the addition of the new US Department of Agriculture (USDA) category of “biopreferred,” i.e. biobased fabricated and formulated products.

Such products are distinctly different from products certified as organic at one of the four levels by the National Organic Program (NOP). Both of these certifications were promulgated by the USDA. The latter, USDA Organic, was developed to certify agricultural products, clearly the domain of USDA, while the former was initially developed to drive federal procurement practices in a more sustainable direction. This more recent biopreferred standard now anoints a wide variety of consumer products, including personal care items such as hand cleansers, sanitizers, lip products and more recently, hair care, as presumably more sustainable for the environment.

To be designated as biobased, a consumer product must simply meet the requirement for what portion of its content is derived from a biological origin. Percentages for each consumer category varies extensively: carpets 7%, towels 12%, glass cleaners 49%, lip products 82%, shampoos 66%, conditioners 78%, etc.5 The jurisdiction here appears to span several agencies including the US Food and Drug Administration (FDA), the US Environmental Protection Agency, and the US Consumer Product Safety Commission. With this new biopreferred standard, the USDA likely does not imagine it could be opening another Pandora’s box as it did with the NOP certification since this standard was developed for farm and derivative food products and is therefore difficult to apply to personal care ingredients and products—hence the promulgation of the aforementioned NSF/ANSI 305 standards for personal care products containing organic ingredients.

The personal care industry is aching for ways to market its products as green—whether they are truly sustainable, milder to the skin, or simply derived from natural origins. Therefore, the new biopreferred standard presents marketers with a unique product positioning especially if there
is a government agency that sanctions the claim because even with the continued antigovernment rhetoric in the media, consumers still trust government agencies as a credible arbiter of advertising claims.

At the Bench
From a pragmatic perspective, this column aims to address what materials consumers may accept and product developers can use to formulate natural hair care products. Most hair care products fit into what could be considered a holistic product paradigm, meaning the whole product itself delivers consumer benefits. This is different from the drug delivery paradigm for personal care formulas, wherein a defined set of actives such as sunscreens, antioxidants, anti-acne and anti-aging materials, etc., deliver the desired benefits. Antidandruff shampoos as well as, arguably, permanent waves or hair colorants also fall into this latter category. In this paradigm, the active ingredients perform a function and the surrounding product is an optimized vehicle or package that carries those goods to the “address” on the label—i.e., the skin, scalp or hair shaft—to deliver the desired benefits. The presumed benefits that accrue from the product feature, in this case the feature of being natural, are enhanced safety or mildness.

These two product development paradigms are, in a sense, arbitrary distinctions, with the lines blurred for many products but they do provide some direction as to the strategies for both goal-directed formulating on the front end and claim substantiation testing on the back end. By examining traditional hair care categories for their critical performance ingredients, formulators can determine what functionality is potentially available from the use of natural ingredients. Some benefits may be more difficult than others to provide through natural ingredients since they were designed into the synthetic molecules in a structure-function approach.

**Shampoos**: Shampoos, for all their ancillary benefits, are primarily meant to cleanse the hair. While the actual amount and type of surfactant necessary to promote the roll-up mechanism of soil and oil removal from fibers is quite minimal, the current consumer is looking for copious foam; in fact, it has been observed that many Asian consumers seek products whose foam density gives a “white glove” appearance on the hands during use. Therefore, the industry is compelled to come up
with natural dense and high foamers. One type of natural surfactant found in a few plant varieties is the saponins, steroidal glycosides that readily generate foam in water. They work well for beverages where they are generally recognized as safe (GRAS) and impart copious foam to frothy drinks. However, in personal care, the do not impart a lather as rich as consumers expect from their shampoos at conventional use levels of less than 1%.

Of course, formulators could hark back to the old fashioned technology of liquid soaps by using unsaturated vegetable oil fatty acids, as some pioneers in natural products still do. Soaps made with oils from unsaturated fatty acids, such as olive, the traditional castile soap in Renaissance Spain, or hemp oil, can remain clear in a concentrated solution. Mixed with coconut to enhance the lather, these liquid soaps do cleanse well but they experience solubility problems in hard water. One suggestion would be to add natural chelating agents such as phytate salts or inositol hexaphosphate to chelate with the divalent calcium and magnesium ions. However, pH effects may limit the usefulness of such techniques. Some such commercial agricultural sources include rice and soy.

If natural certification by bodies such as Ecocert is the standard followed, the surfactant choice becomes much wider, encompassing anionics such as acyl glutamates, acyl hydrolyzed protein salts and even alkyl sulfates and sulfosuccinates; amphoterics like the cocoamphoacetates; and nonionics in the alkyl glucoside family. Ranges of mild, high-foaming products can be formulated but the biggest concern is how to thicken these shampoos effectively and cheaply.

Formulators cannot get away with the conventional salt-thickening method used in many mass market, dollar-a-bottle shampoo variants but there are some natural polymers, such as xanthan gum, that can successfully be used. Work has also been done using magnesium sulfate (Epsom salts) in combination with fatty amphiphiles such as glyceryl laurate to thicken glutamate cleansers by building surfactant association structures akin to those using the cheaper monovalent salts.

Hair conditioners: Hair conditioners deliver the eponymous benefit of hair conditioning, but what exactly does this mean? Looking at how one actually tests hair conditioning—i.e., via tress testing and half-head salon testing—can provide formulators with answers. In
Hair Care

answer to these tests, key conditioner benefits would therefore include reducing the force necessary to comb through wet and dry hair fibers as well as reducing the surface charge on hair fibers, in this case excess negative energy, to reduce electrostatic repulsion and the macroscopic appearance of fly-away. And what better way to impart these effects than applying a species that has both a positive charge and a long molecular chain of low intermolecular attractive forces, such as hydrocarbon or silicone polymers. In the conditioner arena, these would be cationic surfactants, exemplified by quaternary ammonium salts or quats, but these are severely restricted by most private natural certifiers.

However, formulators can look to amino acid derivatives as a way out of this dilemma. Two examples are PCA ethyl cocoyl arginate and brassicyl isoleucinate esylate, which can provide hair conditioning. Like their parent compounds, i.e. proteins and amino acids, they are naturally amphoteric. Thus, the pH of the system governs their functionality, as dictated by their isoionic points. Although not promoted as heavily as in the past, the acyl derivatives of amino acids and proteins may eventually be the shining light of naturals for hair treatments—both for cleansing and conditioning. Combinations of vegetable oils and jojoba oil and other emollients also find their way into hair conditioners, as well as lecithin, usually of soy origin, all of which are available in NOP organic versions. These materials have some substantivity to the hair cuticle, virgin hair more than damaged, and can serve as a friction-reducing film on the hair shaft. These ingredients are also seen in conditioning shampoos and body washes, although most of their conditioning effects are washed down the drain.

It is important to remember that when looking at natural derivatives, some simple naturals can be derived via synthetic routes. Glycine, the smallest amino acid, for example, is abundant in nature but it is difficult to distinguish the natural from the synthetic; having no substituent on the carbon between the carboxyl and amine groups, it does not have positive and negative optical isomers as all the other proteogenic amino acids do. One cannot tell the feedstock source simply because it is not chiral. The same is also true for glycerol-based derivatives; there are both synthetic and naturally derived versions from vegetable oils and fats, as well as natural biological building blocks of animal origin, so formulators may want to ask their suppliers to certify the source.
Further, the same can also be an issue also with preservatives and fragrances. Some nature-identical preservatives are allowed under certain certification systems, e.g. NaTrue, but are only allowed under NSF/ANSI 305 if they are derived from non-petrochemical feedstocks. Fragrance also can have natural roots, and many flavor and fragrance houses can provide natural fragrances. Combinations of related essential oils, many available as NOP Organic, can form pleasant compositions but professionally developed natural fragrances are better suited to most products. Aromatic extracts of fruits and flowers are also available if that is the chosen marketing direction.

There are, however, severe limitations in relation to color since many colors extracted from plants are not approved for cosmetic use, even if they are approved for food and drug use. The soluble dyes that can be used include caramel, annatto, beta-carotene and carmine from the Mexican cochineal insect. Formulators are not likely to use inorganic pigments such as titanium dioxide, iron oxides or chrome oxides, which go into color cosmetics, in hair care. There is also the unique copper chelate disodium EDTA-copper, which is only approved for use as a shampoo colorant but unfortunately it is not natural.

**Styling aids:** Styling aids and hair sprays depend upon the film-forming or simple adhesive properties of their dry residues. Fiber bundles typically are either coated with a solution of polymer or sprayed with a mist of droplets that “spot-welds” the fibers together, as numerous hair chemists have metaphorically quipped, to affect the style and freeze it in place. Such polymers can come from natural sources–either carbohydrate- or protein-based. The drawback here is their reduced humidity resistance. Proteins such as corn zein and carbohydrates such as plant gums, e.g. acacia or Arabic gum and pectin, currently are used. In addition, a unique thickening combination of xanthan and konjac mannan carbohydrates reportedly yields clear gels, and potentially could be one alternate to the synthetic polyacrylate carbomer in making clear gels. Finally, to modify flexibility and reduce flaking, glycerol may be considered as a universal plasticizer and other glycols, such as fermentation-sourced 1,3 propylene glycol, can be used.

In addition, besides being a good cosolvent in water-based products, ethanol at >15% can be a fail-safe preservative in hair sprays but readers should note the importance of microbial challenge testing the final
formula in all cases. The formula pH and water activity can also provide strategies to aid in preservation with low pH levels where feasible. The use of water activity control as a strategy has been suggested by Steinberg, as water activity can have significant bacteriostatic effects in highly concentrated systems like shampoos but yeast and mold will still be problematic. An instrumental determination of water activity is therefore essential.

Conclusions

A full compendium of natural ingredients for hair care would be difficult to compile at any point in time as more materials are being invented or their utility in personal care discovered every day. Many will gain approval by Ecocert, QAI, NaTrue or the Natural Products Association and become additions to the natural formulators’ palette. A complete volume would be too extensive to catalog here but if product developers simply want to work with Mother Nature as she provides, the palette will be limited to nature-made metabolite, e.g. proteins, lipids and carbohydrates that were found on farms, in fields and in oceans before the advent of organic synthetic chemistry. Otherwise formulators can choose a natural certifier and consistently apply their guidelines.

The future will unfold with new ingredients for natural formulations as green chemistry advances yield new functional ingredients. This consumer need for natural and sustainable technologies will not stifle creativity but instead add a new direction to innovation. The bench chemist should monitor activity in the regulatory arena as the overlap between the FDA, USDA and Federal Trade Commission jurisdiction is worked out; in fact, the Personal Care Products Council has established an Organic/Natural Committee to keep abreast of these developments. In addition, on both the domestic and international fronts, formulators should follow the non-governmental organizations that are promulgating natural standards as these are evolving as well. Good luck!
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Green Formulations: Not All Components Are Equal

A. Cristoni, G. Maramaldi and C. Artaria

Nature has always been a generous source of wellness for mankind. Since ancient times, the healing properties of various plants have represented the first medicines and cosmetics. The study of tribal and native traditions has many times laid the foundation to successfully isolate new and effective cosmetic active ingredients.

Modern functional cosmetics represent valid alternatives to dermatological treatments for preventing the signs of aging, and the plant kingdom can provide many active compounds to counteract those signs, including: skin tone and elasticity loss,\(^1\) wrinkle formation,\(^2,3\) capillary fragility,\(^4\) and increased skin sensitivity.\(^5\)

However, natural ingredients require specific expertise not only in their research, but also in their analysis and formulation. The quality of botanical extracts, which needs to be standardized, is a crucial point for the quality of the final formulation, among others.

**Standardized Extracts**

To demonstrate the efficacy and reproducibility of a botanical active’s variables in a cosmetic formulation, the consistency of the natural extract is a key factor. Reproducibility is also important when considering regulatory aspects aimed to assess the toxicity and tolerability of a cosmetic ingredient.
The consistency of a botanical extract is relatively achievable when dealing with a pure product such as escin or esculin from *Aesculus hippocastanum*; glycyrrhetinic acid from *Glycyrrhiza glabra*; or with a dry extract highly purified up to the isolation of a unique class of molecules such as triterpenes from *Centella asiatica*, flavolignans from *Silybum marianum*, polyphenols from *Vitis vinifera* and anthocyanins from *Vaccinium myrtillus*.

In some cases it is convenient to purify a unique active principle up to 80–90%, whereas in other cases a complete extract of numerous different compounds may be more active than the single isolated molecules. Research in this field is complex and involves not only the identification of the active principle, it also aims to investigate the interactions between the active ingredients and other molecules present in the phytocomplex.6

Different technologies or manufacturing methods may be necessary for different types of extracts but the main parameters include: composition constancy, stability, microbe counting and the limitation of residual solvents and pesticides. These parameters should be carefully monitored as required by health authorities.

The crucial stages of the process include, as a rule of thumb, choosing the raw material first, followed by extraction and purification. While the choice of extraction solvents in the preparation of standardized extracts is an important factor for the finished product quality, the choice of the raw material is pivotal.

From a practical point of view, the botanical source must be thoroughly checked before extraction, as far as botanical and chemical aspects are concerned (see Table 1).

The next phase is the preparation of the extract in standardized conditions, which requires the steps described in Table 2.

Extracts prepared according to the criteria in Tables 1 and 2 can be classified as standardized. Although some of these parameters appear obvious, they can be difficult to achieve. For instance, all the botanical materials must be gathered within a short, specific time period then stored after analysis to avoid the degradation of the active ingredients. In some cases, crops from homogeneous, genetically selected strains of plantules or seeds are grown in controlled agrochemical conditions. Cultivation can be a solution for plants whose harvesting in the wild could endanger the species’ survival.
Table 1. Raw material characteristics and preliminary analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Action to control the parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Part of plant</td>
<td>Botanical identification, macro and microscopic analysis, control of sophisticant and contaminant presence</td>
</tr>
<tr>
<td>Harvesting</td>
<td>Careful selection and control of the region, area and harvesting period</td>
</tr>
<tr>
<td>Storage</td>
<td>Control of harvesting, drying and storage conditions</td>
</tr>
<tr>
<td>Active principle content</td>
<td>Chemical analysis in order to adequately mix different batches</td>
</tr>
<tr>
<td>Heavy metals and pesticides</td>
<td>Chemical analysis in order to discard the polluted batches</td>
</tr>
</tbody>
</table>

Table 2. Standardization and analysis

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Action to control the parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Extraction</td>
<td>Follow a defined method, with specified grinding, solvent, temperature, pressure</td>
</tr>
<tr>
<td>Concentration (if necessary)</td>
<td>Follow defined procedures, with analysis at the key steps of production</td>
</tr>
<tr>
<td>Chemical analysis</td>
<td>Control of the content in active principles, and control of the presence of impurities, heavy metal, pesticides and residue solvents</td>
</tr>
<tr>
<td>Microbiologic analysis</td>
<td>Control of the microbial presence and of pathogen absence</td>
</tr>
<tr>
<td>Stability</td>
<td>Periodical analysis, in order to confirm the extract quality</td>
</tr>
</tbody>
</table>

Safety Issues

From a safety standpoint, the quality of a botanical extract needs to be carefully evaluated both on the raw material itself and within the final formulation—whether it is intended as a topical or oral cosmetic.

Recent evaluations have in fact demonstrated that, besides labelling claims, only a small percentage of commercial products had chemical profiles that complied with their declared content. This research focused
on the commercial preparation of bilberry extract purchased from different countries.

The HPLC method developed and validated in Indena research laboratories was optimized to analyze the content of anthocyanins, the polyphenols that bestow beneficial properties to bilberry extracts. (see Figure 1).

**Bilberry: A Case Study**

Chemical and pharmacological studies of bilberry extract have identified anthocyanosides, also known as anthocyanins, as the major components responsible for the biological properties of bilberry. They have been demonstrated to possess a broad range of activities, including: antioxidant activity,\(^7,8\) antiplatelet aggregation,\(^9\) phosphodiesterase inhibition,\(^10\) interaction with collagen, phospholipids and proteoglycans,\(^11\) a relaxing effect on vascular smooth muscle,\(^12\) and arteriolar vasomotion stimulation.\(^13\)

Bilberry is exploited for its capacity of reinforcing the blood vessel wall: it strengthens capillary walls by linking with the endothelial cell membranes, thus increasing their resistance and reducing capillary permeability by stimulating the synthesis of perivascular tissue constituents. In topical applications, these properties are particularly useful in case of heavy legs or couperose, where microcirculation improvement and capillary tone are crucial to the relief of disorders.

According to Indena research,\(^6\) 40 different preparations containing bilberry, marketed under 24 different brands, were collected in four different countries for analysis. The samples came from the United States, Italy, Japan and Malaysia. The labels indicated three different types of preparations:

- bilberry extracts with a 36% anthocyanin content;
- bilberry extracts with a 25% anthocyanidin content; and
- bilberry extract without content indication.
The analytical work based on HPLC revealed that 25% of the tested products had a different profile from a typical bilberry profile of either an anthocyanins content at 36%, or anthocyanidin at 25%. In fact, 10% did not even contain the active anthocyanins molecules and only 15% were found to possess a sufficient quantity of anthocyanins to be effective, as proven by clinical trials.

The fact also emerged that only 65% of the tested commercial products sold in the United States contained a quantity of ingredients matching the label claim.

Regarding the issue of appropriate labelling, a recent review of the described analytical work highlighted some of the confusing information provided to the final consumer. For instance, the identity of the botanical species *Vaccinium myrtillus*, the only species with a sound tradition of medicinal use and well-documented by the scientific literature, is reported in 60% of labels, whereas the genus *Vaccinium* comprises over 450 species and the part of the plant is indicated on 70% of labels.

It needs to be taken into consideration that different parts of the same plant may have different biological properties. Bilberry leaves, for instance, have been traditionally used as a remedy for diabetes. This is not surprising since bilberry leaves, although they contain few anthocyanosides, are rich in tannins. The active ingredients are not defined on the labels, making it difficult for the consumer to understand the differences between the products. The quantity it contains in either milligrams or as a percentage concentration also is not listed.

**Conclusions**

Callaghan observed that when the cosmetic industry wants to demonstrate how supplements can benefit the skin, it needs to be innovative and address questions relating to safety, toxicity, bioavailability, molecule interactions that control biological function, and age-related physiology.

The commercial preparations that have been analyzed recently highlight differences in content and variations between labelling and actual concentration, revealing a scenario of the herbal preparations that require the development of reliable analytical methods to analyze finished formulations.
It is important for formulators to be aware of the different qualities of natural extracts that may, by all means, affect the quality of the final formulations.

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Navigating the Challenges of Formulating With Naturals

Lakshmi Prakash, Ph.D., and Muhammed Majeed, Ph.D.

A judicious blend of art and science is critical to creating natural cosmeceuticals for use in personal care products. The major challenge is finding ingredients that are compatible with existing formulations. Aesthetics is a particularly important concern. For example, while there is much interest in using natural botanical extracts in cosmetic preparations, a too-dark color, a gritty texture, ingredient instability, poor absorption of actives, or dispersibility problems could render the “healthy and natural” ingredient unattractive. Additionally, the safety and efficacy of natural ingredients need to be established in order to enable their use in finished personal care products.

Challenges in Innovating

Color issues: Natural ingredients for antiaging skin care are prepared from botanicals with a long history of traditional cosmeceutical use, such as skin lightening, skin smoothing and antimicrobial applications, although the term itself is of recent origin. Botanicals are rich in phenolic and other pigments including carotenoids, flavonoids and related compounds, and often some of the healthful properties of these natural materials reside in the pigments themselves. An example is turmeric, a culinary spice with a tradition of topical use in South Asia. The active compounds in this case are the yellow curcuminoids that also are used as a natural colorant. This brilliant
yellow color, however, does not blend well with currently manufactured personal care products. The end user is concerned about the unappealing yellow color staining the skin.

Scientific developments such as extraction processes and derivatization techniques have enabled a method to extract the mixture of biologically active curcuminoids from turmeric roots and convert them into colorless biologically active tetrahydrocurcuminoids. Such a composition finds versatile applications in personal care products, particularly in the antiaging category.

Tetrahydrocurcuminoids have been found to efficiently inhibit protein cross-linking and provide skin-lightening action as well as provide antioxidant and bioprotectant properties. This discovery is the subject of a recently granted U.S. patent.\(^1\)

Tetrahydrocurcuminoids offer additional functional antioxidant benefits in protecting fat-based compositions from oxidation. In laboratory studies,\(^2\) tetrahydrocurcuminoids were found to quench free radicals more efficiently than the commonly used synthetic antioxidant, butylated hydroxytoluene (BHT).

From a safety point of view, the bioprotectant role of tetrahydrocurcuminoids is further enhanced by its low toxicity, (oral LD\(50\) is 5000 mg/kg) with a 0.00 irritation score in a skin patch test.\(^3\) Turmeric root, the source of tetrahydrocurcuminoids, is listed by the U.S. Food and Drug Administration (FDA) as an herb generally recognized as safe (GRAS) for its intended use as a spice, seasoning and flavoring agent.\(^4\)

**Dispersibility:** Botanicals often are difficult to use in formulations because of their poor solubility or dispersibility in acceptable solvents. In such cases, the formulator faces a challenging task that sometimes requires modifications to the formulation process itself. The order of addition of ingredients, the type of solvents used, temperature and pH conditions, the nature of the mixing process and several other factors influence dispersibility.

*Boswellia serrata* for example, has been used in the ayurvedic system of medicine to manage inflammatory conditions (see *Boswellia Serrata* in Antiaging).
Boswellia serrata in Antiaging

Olibanum, the resin from the Boswellia species, has been used as incense for centuries. Its major use today is as a fixative in perfumes, soaps, creams lotions and detergents. In India, the gum resin exudates of Boswellia serrata and has been used in the ayurvedic system of medicine in the management of several inflammatory conditions.

Inflammation is considered to be the prime cause in aging, an inflamed site forming a micro-scar that over time develops into a wrinkle or blemish. Inflammatory mediators such as leukotrienes and prostaglandins, cytokines and growth factors target skin texture, integrity and tone. Containing inflammation at its roots is therefore an effective antiaging strategy.

The active boswellic acids reside in the gum resin from the tree, which is a difficult material to formulate, and the gum constituents may irritate the skin. Natural extract manufacturers have developed efficient extraction processes that produce a composition rich in boswellic acids in a powder form. Such an ingredient can be conveniently used in formulations for soaps, lotions and cosmetic creams as an anti-inflammatory ingredient (see Formula 1)—however, the powder must be dispersed well during the formulation process. Optimal proprietary methods for formulation have been developed after extensive experimentation.

Products tested containing 5% of a standardized extract from the gum resin\(^a\) did not produce any irritation or sensitization in standard patch tests.\(^5\)

**Stability issues:** Retaining the biological activity of natural ingredients through raw material preparation, processing, extraction, packaging and storage presents a myriad of challenges.

Nutrients in natural materials such as vitamins, growth factors, amino acids, flavonoids, pigments and essential oils are susceptible to degradation on contact with oxygen or exposure to suboptimal temperature and pH conditions.

An example is young or “green” coconut water—a reservoir of nutrients and growth factors. Green coconut water is the liquid

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\(^a\) Boswellin (INCI: Boswellia serrata extract) is a registered trademark of Sabinsa Corp.
endosperm of coconut (*Cocos nucifera* L), which is a refreshing natural drink in the tropics and traditionally used as a health and beauty aid. Natural coconut water is rich in proteins, amino acids, sugars, vitamins, minerals and growth hormones that are essential to promote tissue growth. Laboratory researchers use the material as a supplement in media for the growth of plant tissue cultures.

### Formula 1.
**Cream formulation with *Boswellia serrata* extract**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>A.</td>
<td>Water (aqua) 59%–60%</td>
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<tr>
<td></td>
<td>Carbomer 0.25%–0.27%</td>
</tr>
<tr>
<td>B.</td>
<td>Glycerin 4.0 Methylparaben 0.2</td>
</tr>
<tr>
<td></td>
<td>Edetate sodium 0.01</td>
</tr>
<tr>
<td>C.</td>
<td>Cetyl alcohol 3.5</td>
</tr>
<tr>
<td>D.</td>
<td>Stearyl alcohol 3.5</td>
</tr>
<tr>
<td></td>
<td>Stearic acid 6.5</td>
</tr>
<tr>
<td></td>
<td>Glycerol steareate 2.5</td>
</tr>
<tr>
<td></td>
<td>PEG-100 steareate 2.5</td>
</tr>
<tr>
<td></td>
<td>Isopropyl palmitate 6.0</td>
</tr>
<tr>
<td></td>
<td>Vitamin E acetate 1.0</td>
</tr>
<tr>
<td></td>
<td>Dimethicone 0.1</td>
</tr>
<tr>
<td></td>
<td>Propylparaben 0.1</td>
</tr>
<tr>
<td></td>
<td>Vitamin A palmitate 0.1</td>
</tr>
<tr>
<td></td>
<td>Ascorbyl palmitate 0.2</td>
</tr>
<tr>
<td>E.</td>
<td><em>Boswellia serrata</em> extract 5.0</td>
</tr>
<tr>
<td>F.</td>
<td>Water (aqua) 2.0</td>
</tr>
<tr>
<td></td>
<td>Triethanolamine 0.4</td>
</tr>
<tr>
<td>G.</td>
<td>Imidazolidinyl urea 0.3</td>
</tr>
<tr>
<td></td>
<td>Water (aqua) 1.0</td>
</tr>
</tbody>
</table>

**Procedure:** Mix A under propeller agitation until dissolved. Add B to A and blend. Begin heating to 72°C–77°C and continue mixing until completely dissolved. In a separate container, charge C and add D to C in order. Heat CD to 72°C–77°C until dissolved. Mix CD with AB, maintaining 72°C–77°C. Add E to batch under propeller agitation. In a separate container, combine F until dissolved and mix with batch. Keep mixing until completely dissolved while maintaining 72°C–77°C. In a separate container, combine G until dissolved and add to the main batch. Mix and cool to 35°C–40°C and package.

Coconut water is useful in hair care formulations and in topical preparations to rejuvenate, nourish, condition, soothe and moisturize the tissues. However, its short shelf life and sensitive nature of the inherent actives make it difficult to use the material in cosmetic formulations. A freeze-drying process has been developed to retain
the activity of coconut water components. The process produced a light tan-colored powder consisting of coconut water solids that readily blends into cosmetic preparations. In *in vitro* irritation studies, a product formulated with the ingredient was found to be non-irritating.

**Skin permeation:** The efficacy of actives depends upon their skin permeation capabilities. Selective nutrient absorption by the skin is an important physical property of the skin. This selective process begins with the stratum corneum (SC). The function of this barrier is related to the unique composition of the lipid moiety in the epidermis. The intercellular lipids mediate transdermal delivery of both lipophilic and hydrophilic molecules. Research shows that regulating the composition of intracellular lipids in the skin can increase or decrease the bioavailability of nutrients.

Besides the modification of skin lipid composition, there are several strategies to improve topical nutrient bioavailability. Improvement can be accomplished by supersaturation of the delivered ingredient. The delivery formulation also may contain ingredients that decrease the diffusional (electrostatic) resistance of the lipid bilayer to the passing molecule. Topical liposome preparations are effective penetration enhancers for the delivery of biological compounds, probably due to their role in increasing cell membrane fluidity. In addition, an increase in blood supply to the skin can enhance absorption of delivered nutrients.

Historically, a number of chemical-penetration enhancers have been used to enhance the uptake of actives. These include: solvents such as dimethyl sulfoxide (DMSO), ethanol and other alcohols; glycols such as propylene glycol; fatty acids such as oleic acid; and detergents such as sodium lauryl sulfate, polyoxyethylene lauryl ethers, and chaotropic agents such as thioglycolate, urea, and mercaptoethanol.

As such, they also have the potential to cause damage to the SC and to increase the probability of irritation. Most of these agents work by perturbation of the intercellular lipid bilayers present in the SC.

Therefore, there is a need for compounds of natural origin with low irritancy and minimal side effects that can be efficiently combined

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*b Cococin (INCI: Cocos nucifera (coconut) fruit juice) is a registered trademark of Sabinsa Corp.*
with nutrients to enhance the uptake and utilization of such active molecules.

An innovation in enhancing topical delivery of natural actives is available in the form of a proprietary extract obtained from black pepper fruits, a common culinary spice. When added in small amounts (0.01%–0.1%) to cosmetic formulations, tetrahydropiperine, the active principle, enhances the uptake and delivery of other actives in the formulation. Poorly absorbed botanicals, therefore, can be made more “bioavailable” with this ingredient.7

**Quality, safety and efficacy:** Herbal raw materials available commercially as powders and extracts often do not meet global standards of quality, efficacy and safety. To preserve the authenticity and credibility of such products, it is important that the ingredients therein contain adequate amounts of biologically active principles that manifest the desired biological functions.

Plant materials pose several challenges in standardization. Natural products are complex matrices with a number of active principles varying widely in content and type, based on geographical origin, cultivation and collection practices, and processing and storage conditions. This often leads to variations in potency, label ambiguity and related problems in finished cosmetics.

Compositional consistency of botanical extracts in terms of active principles is the key factor in ensuring potency and sustaining consumer confidence. Marker compounds are chemicals proven to be characteristic of botanicals and endowed with validated health benefits. Chemical fingerprints using chromatography and spectrophotometric methods, in combination with bioassays, are the accepted methods to ensure the presence of marker compounds in botanical materials.

A botanical’s active principle may concentrate in a specific location in the plant and manufacturers often use combinations of plant materials in preparing finished extracts. Contaminant levels, including heavy metals, pesticide residues, extraneous matter and genetic modification aspects also need to be considered. The complexity of these challenges is exacerbated by mislabeling in the commercial marketplace.

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7 Cosmoperine (INCI: Tetrahydropiperine) is a registered trademark of Sabinsa Corp.
Organic vs. Natural

According to the U.S. Department of Agriculture’s (USDA) National Organic Program (NOP), the term organic may be used on product labels when certain conditions are met.¹

**100% organic:**
- This designation may be used for agricultural products that are composed of a single ingredient such as raw, organically produced fruits and vegetables and products composed of two or more organically produced ingredients, provided that the individual ingredients are, themselves, wholly organic and produced without any nonorganic ingredients or additives. (Only processing aids that are, themselves, organically produced, may be used in the production of these products.)

**Organic:**
- Products labeled or represented as organic must contain, by weight (excluding water and salt), at least 95% organically produced raw or processed agricultural product.
- Up to 5% of the ingredients may be nonagricultural substances and, if not commercially available in organic form, nonorganic agricultural products and ingredients in minor amounts (i.e., spices, flavors, colorings, oils, vitamins, minerals, accessory nutrients, incidental food additives).

**Made with organic ingredients:**
- Multiingredient products containing by weight or fluid volume (excluding water and salt) between 70%-95% organic agricultural ingredients may be designated as “made with organic [specified ingredients or food group(s)].” Up to three organically produced ingredients or food groups may be named in the phrase.

The term natural, according to the National Consumer’s League (NCL), is not regulated by the FDA as far as the use of the word on personal care or cosmetic products.² The FDA’s Office of Cosmetics and Colors has, however, produced consumer information regarding the natural claim for personal care products. Products claiming to be all natural or plant-derived may include more than just natural ingredients or plant products.

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Authentication of plant materials used to manufacture cosmetic ingredients is critical. Selecting appropriate extraction and purification processes is important as this reflects heavily on the quality of finished extracts. To avoid skin irritation and sensitization, solvent residues and other contaminant levels in finished extracts should be minimized.

**Meeting These Challenges**

In the rapidly growing market for natural antiaging cosmetics, application-oriented product development goes a long way in facilitating the introduction of traditionally used botanicals into conventional formulations. The initial challenge is to innovatively transform plant materials into safe and efficacious ingredients for functional cosmetics. Once this is achieved, the next step is to comprehensively address global regulatory issues and nurture consumer confidence through consistent quality management. Furthermore, in vitro testing methods for safety and efficacy need to be optimized to facilitate cruelty-free product development.

Nature provides a plethora of options to support healthy aging. Blending traditional knowledge with modern science results in innovative approaches to the effective use of plant-based materials in contemporary personal care formulations.

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