Formulation of natural shampoos

A. R. Mainkar and C. I. Jolly
Department of Pharmacognosy and Phytochemistry, Principal K. M. Kamdani College of Pharmacy, Worli, Mumbai-400018, India

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Synopsis

Formulating cosmetics using completely natural raw materials is a difficult task. The challenge lies in selecting materials that can be rationally justified as ‘natural’ and formulating them into cosmetics whose functionality is comparable with their synthetic counterparts.

The present paper focuses on the formulation of completely natural shampoos, their evaluation and comparison with commercial herbal shampoos. Attention is drawn to the fact that, due to the ambiguous definition of the word ‘natural’, several so-called natural cosmetics are available in the Indian market. It is up to the cosmetic chemists themselves to promote and encourage the development and use of truly natural cosmetics.

Résumé

La formulation de produits cosmétiques utilisant des matières premières complètement naturelles est une tâche difficile. La difficulté réside dans le choix de matières qui peuvent rationnellement être démontrées comme "naturelles" et de les formuler en produits cosmétiques dont l'utilisation est comparable à celle de leurs contreparties synthétiques.

Le présent article s'intéresse à la formulation de shampoings entièrement naturels, à leur évaluation et à la comparaison avec les shampoings végétaux du commerce. On attire l'attention sur le fait que, en raison de la définition ambiguë du mot "naturel", plusieurs produits cosmétiques dits naturels sont disponible sur le marché indien. C'est aux chimistes cosmétiques eux-mêmes de promouvoir et encourager le développement et l'utilisation de produits cosmétiques réellement naturels.

Introduction

Natural cosmetics are popular all over the world, as they convey the impression of having better purity, safety and efficacy. Many shampoos are available in the Indian market under the label of ‘natural’, ‘herbal’, etc. However, these formulations are based on synthetic detergents and other chemical additives and contain herbal extracts added more for their marketing value than for their efficacy. The general feeling among consumers is that a good shampoo is one that foams very well. To cater to this consumer expectation, formulators may add excessive amounts of detergents in the shampoos. The most commonly used surfactant is sodium lauryl ether sulphate (SLES), which is manufactured by the ethoxylation of sodium lauryl sulphate (SLS) using ethylene oxide. In this case, residual ethylene oxide, dioxane and acetaldehyde may be present as impurities in the surfactant [1]. The most popular conditioning agents used in shampoos today are cationic polymers and surfactants, some of which may present the risk of nitrosamine development. Nitrosamines are known to be hazardous to health. Formaldehyde or formaldehyde-based chemicals may be used as preservatives in the formulation, which may cause adverse effects such as skin irritation/sensitization.

In view of the above scenario, the present work was aimed at the development of completely natural shampoos and their comparison with the commercial ones.
However, formulating a shampoo using all natural raw materials is a formidable task [2]. The challenge lies not only in selecting the materials that can be rationally justified as ‘natural’, but also in matching the performance characteristics of the formulation with the synthetic ones available in the market.

Requirements of a natural shampoo

A modern shampoo must be multifunctional and meet the following criteria:
- mild detergency
- foaming comparable with retail products
- good conditioning
- adequately preserved
- aesthetically appealing.

As there are no set standards regarding what constitutes as a ‘natural’ material, there are as many definitions of natural as there are products available. In our view, a natural shampoo must conform to the following:
- No hazardous chemicals, especially ethoxylates/nitrosamines/formaldehyde
- Only plant or plant-based surfactants
- Completely natural additives, especially preservatives.

Formulation strategy

Choice of detergents

Most shampoos contain a mixture of two or more surfactants in a concentration ranging from 25 to 30%. Although such a high concentration of detergents is not required in a shampoo, formulators use them nonetheless to generate excessive foam. In effect, many modern shampoos can be harsh ‘oil-strippers’ and leave the hair feeling dry and unmanageable [3]. It is extremely difficult to obtain a single natural material that would be milder and safer than the synthetic ones, and at the same time would compete favourably with its foaming, detergency and wetting powers. We considered the use of saponin-rich plants for this purpose. The pericarps of Sapindus mukorossi, commonly known as soapnut or ‘reetha’, have traditionally been used for washing hair, so we decided to perform preliminary investigations on them. The results showed that using the water extract of the material alone was inadequate in performing the desired functions. It was therefore decided to extract the saponins from the pericarps and incorporate them in the formulation. The saponins were extracted by percolation of the powdered pericarps of reetha using butanol [4]. Evaporation of the solvent under reduced pressure provided the saponins in a powdery, non-hygroscopic form, which could conveniently be incorporated in the formulations. To complement its activity, we used another plant-based surfactant, alkylpolyglucoside, which is milder and much safer than the conventional surfactants [5].

Both the materials were used in different concentrations and the combination giving the best results in detergency, foaming and wetting tests was used in the formulations.

Additives

Additives play an important role in defining the performance, stability and aesthetic appeal of any cosmetic formulation. A good shampoo must have adequate viscosity to facilitate removal from the bottle but must not drip down from the hair during use. A variety of natural materials is available for use as viscosity builders. We chose xanthan gum, as it shows pseudoplastic behaviour and forms clear solutions.

The choice of a natural chelating agent and antioxidant is limited. We have used citric acid obtained by biofermentation for this dual purpose, as well as to reduce the pH to the desired level. The pH of shampoos is known to affect the quality of hair [6]. Between pH 4–6, the normal charge distribution of hair remains unchanged, the hair is least swollen and has its maximum wet strength. To maintain a balance between maximum wet strength and minimum eye irritation, we have maintained the pH of our formulations at 5.5. Preservation of an aqueous formulation containing natural raw materials is extremely important. However, choosing a natural antimicrobial substance for this purpose is an arduous task. The literature is full of mentions of natural materials having antimicrobial activity, but it is not easy to predict their performance for a given system. In effect, each substance must be challenge tested to see how effective it is in that particular formulation. The saponins of reetha have been reported to be antimicrobial in nature [7]. Alkylpolyglucosides are also known to be active against certain species of bacteria. These reports encouraged us to try and formulate a ‘self-preserving’ formulation.
the water activity of the system, sodium chloride was added. We envisaged that the antimicrobial nature of the active ingredients, along with the physicochemical parameters such as reduced water activity and acidic pH would be successful in preventing the growth of microorganisms [8]. To test this hypothesis, a ‘basic cleanser’ (i.e. a formulation with only cleansing activity and no conditioning effect) was formulated and subjected to preservative challenge test. The formula (patent pending) for the basic cleanser was as follows:

- Saponins 10%
- Alkapolyglucoside (Plantacare 2000 UP, Henkel KgaA, Germany) 10%
- Xanthan gum 1%
- Sodium chloride 7.5%
- Citric acid solution q.s. to pH 5.5
- Essential oils q.s.
- Distilled water q.s. to 100%

This formulation was challenged by the linear regression method [9]. The microorganisms used for the test were Staphylococcus aureus, Pseudomonas aeruginosa, Escherichia coli, Candida albicans and Aspergillus niger.

Saline solutions 10^5 CFU mL^-1 were used as the stock solutions of each culture. Of this stock solution 0.1 mL was inoculated into 10 mL of the product. One millilitre of a 10^-2 dilution was used for plate count. A control was run similarly using 10 mL of water. After incubation for 24 h, the plate count was taken. Although the control plates showed growth of the organisms, the test plates did not. This implied that the preservative was not inactivated by a 10^-2 dilution. Hence the experiment was repeated using a 10^8 CFU mL^-1 stock solution and using a 10^-4 dilution. However, the test plates still failed to recover the organisms. The same phenomenon was observed in the case of all five organisms tested. Hence, we concluded that the product was not likely to be contaminated by the test organisms [10].

The results of the other evaluations are presented in Table I. Five marketed herbal shampoos were also evaluated similarly. The protocols for the tests and details of the marketed shampoos are discussed elsewhere [11].

### Conditioning agents

There is a plethora of natural materials, which have traditionally been used as conditioning agents for hair. We chose seven plants that are most commonly used for conditioning in retail products and tested their efficacy. The plants chosen were Aloe vera, Acacia concinna, Centella asiatica, Eclipta alba, Emblica officinalis, Nardostachys jatamansi and Hibiscus rosa-sinensis. In case of aloe, the fresh gel extracted from the leaves was used. For all other plants, water extracts were prepared and incorporated in the basic cleanser at different concentrations. The formulations were then evaluated for

### Table I Evaluation of shampoos

<table>
<thead>
<tr>
<th>Tests</th>
<th>Laboratory shampoos</th>
<th>Commercial shampoos</th>
</tr>
</thead>
<tbody>
<tr>
<td>Detergency (% sebum removal)</td>
<td>61.14</td>
<td>61.1-60.12</td>
</tr>
<tr>
<td>Foam volume (mL)</td>
<td>159</td>
<td>152-168</td>
</tr>
<tr>
<td>Foaming time (s)</td>
<td>130</td>
<td>Rich, dense, creamy</td>
</tr>
<tr>
<td>Surface tension (dynes cm^-1)</td>
<td>37.1</td>
<td>32.3-37.7</td>
</tr>
<tr>
<td>Viscosity (poise)</td>
<td>80</td>
<td>20-60</td>
</tr>
<tr>
<td>pH</td>
<td>5.5</td>
<td>5.1-7.6</td>
</tr>
<tr>
<td>Clarity</td>
<td>Clear</td>
<td>Crystal clear</td>
</tr>
</tbody>
</table>

### Table II Conditioning of shampoos

<table>
<thead>
<tr>
<th>Shampoo formulation</th>
<th>Protein loss (mg g^-1 of hair)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shampoo A: 25% Aloe vera gel</td>
<td>0.225</td>
</tr>
<tr>
<td>Shampoo B: 10% Acacia concinna ext.</td>
<td>0.287</td>
</tr>
<tr>
<td>Shampoo C: 10% Centella asiatica ext.</td>
<td>0.349</td>
</tr>
<tr>
<td>Marketed shampoos</td>
<td>0.547-0.786</td>
</tr>
</tbody>
</table>

conditioning efficacy by protein loss measurements on post-shampoo combing [12]. The formulations that gave the best results are presented in Table II.

Formulation A (which contains 25% aloe vera gel in the basic cleanser) was subjected to stability testing. After 6 months at 37 °C and 45 °C the product remained stable. The other two formulations were not tested, but are expected to behave similarly.

**Discussion**

As seen from the results, it is possible to formulate a completely natural shampoo that is better than the synthetic ones. The commercial herbal shampoos may contain excessive detergents, which can strip the hair of up to 80% of the oil and thus damage the hair. Using a mild detergent in our shampoo we have ensured that this does not happen. Instead of using cationic conditioners we have used aloe vera gel and other plant extracts to provide the conditioning effects. These are not only safer than the chemical conditioning agents, but also greatly reduce the protein loss during combing. The pH of the shampoo has been adjusted to 5.5, to retain the acidic mantle of scalp. Synthetic preservatives have sometimes been the cause of adverse effects among consumers. We have used the physico-chemical approach to preservation and by formulating a ‘self-preserving’ shampoo, have avoided this risk posed by chemical preservatives. However, the aesthetic attributes, such as lather and clarity, of the laboratory shampoo are not comparable with the market shampoos. The foam volume is on a par, but the feel of the foam is different, the natural formulation forms a loose lacy foam structure as compared to the dense lather of the marketed shampoos. Although the retail products do not fare so well in the tests conducted by us, they enjoy market popularity, especially if they foam well. This is mainly due to the false notion among consumers that ‘a shampoo that foams well, works well’, and no real effort on the part of manufacturers to counter this fallacy.

In the present scenario, it seems improbable that a natural shampoo, although better in performance and safer than the synthetic ones, will be popular with the consumers. A more radical approach in popularizing a natural shampoo would be to change the consumer expectations from a shampoo, with emphasis on safety and efficacy. Formulators must play an active role in educating the consumers about the potential harmful effects of synthetic detergents and other chemical additives present in shampoos. There is a strong need to change the consumer perception of a good shampoo and the onus lies with the formulators.

**Acknowledgement**

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**References**


