Formulation and Evaluation of a Shampoo Containing Lipids of Origanum Cyclon Powder

ORIGANUM SİKLON TOZU LİPİTLERİNİ İÇEREN BİR ŞAMPUAN FORMÜLASYONU VE DEĞERLENDİRİLMESİ

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Summary

Lipids of *Origanum* cyclon powder are potential cosmetic raw materials owing to their high fatty acid content. Study on the efficacy of this material when incorporated into a shampoo was evaluated physico-chemically and dermatologically. Following formulation studies, foam characteristic, rheology and stability tests of the preparation have been performed. In a monadic product test, sensory evaluation test comprimising several attributes of the shampoo prepared was achieved using 15 volunteers. At the same period, hair moisture and scalp sebum was measured objectively. Irritation was also determined using patch test.

An acceptable, nonirritant and stable clear liquid shampoo has been formulated which was found to be satisfactory as a cleansing preparation. However, some attributes need to be modified. Lipid extract of *Origanum* cyclon powder seems to add moisture and sebum especially at the end of the first week of use. It is a promising cosmetic raw material which can be incorporated into skin care preparations.

Key Words: *Origanum* cyclon powder, Shampoo, Formulation, Characterization, Evaluation

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Özet

Yüksek yağ asidi içeriklerinden dolayı, *Origanum* siklon tozu lipitleri kozmetik değeri olabilecek hammaddelerdendir. Şampuan içine eklenen bu maddenin etkenliği, fiziko-kimyasal ve dermatolojik olarak incelenmiştir. Formülasyon çalışmalarının ardından, bitmiş preparatın köpük özellikleri, reolojisi ve stabilitesi saptanmıştır. Monadik ürün testinde, şampuana ait birçok kullanım özelliğinin subjektif olarak değerlendirilmesi 15 gönüllü üzerinde gerçekleştirilmiştir. Ayni zaman aralığında, saçın nemi ve saçlı derinin sebumu objektif olarak ölçülmüştür. Bunların yanısıra, yama testi kullanılarak irritasyon belirlenmiştir.

Temizleyici olduğu saptanan, kabul edilebilir, nonirritan ve kararlı bir berrak sıvı şampuan formüle edilmiştir. Ancak bazı kullanım özellikleri iyileştirilmelidir. *Origanum* siklon tozu lipit ekstresinin, özellikle 1 hafta kullanımın ardından nem ve sebuma katkı sağladığı görülmektedir. Bu madde, cilt bakım preparatlarına sokulabilecek, gelecek vaat eden bir kozmetik hammaddesidir.

Anahtar Kelimeler: *Origanum* siklon tozu, Şampuan, Formülasyon, Karakterizasyon, Değerlendirme

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A good cosmetic chemist must be aware of the application characteristics of a preparation which has been formulated and whose physical and chemical properties have been determined.

Cleaning the hair is not only a practice essential for personal hygiene, but is also part of a cosmetic care for satisfactory appearance. Most shampoos are preparations of either aqueous solutions, emulsions or dispersions, containing cleansing agents, fragrances, and other additives such as thickeners, foam builders and active agents. Synthetic surfactants are the prime cleansing agents in modern shampoos.

Origanum cyclon powder is the discarded fraction of the plant obtained during grinding process and was used in this study with economical concerns. In this study, ethanolic lipid extract of *Origanum* cyclone powder collected in the cyclon during the pilot scale process of *Origanum* was formulated as a shampoo and evaluated physico-chemically and dermatologically to investigate the cosmetic acceptability of the extract because of its potential content.

Materials and Methods

Materials and Apparatus

Sodium lauryl ether sulfate (Texapon N40®), cocoamide diethanolamine (Comperlan KD®) and cocoampho diacetate (Dehyton G®) were all supplied from Henkel, Turkey. Sodium chloride and citric acid were from E. Merck, Germany. Water was used immediately after distillation.

Mechanical stirrer (Heidolph RZR 2051); water bath (GLF 1052); pH-meter (Schott CG 841); rheometer (Brookfield DV III); stability cabins (Aymes); Skin pH-Meter, Skin Sebumeter, Mexameter (all Courage&Khazaka) were the apparatus used.

Methods

Preparation of the Shampoo

Lipids of *Origanum* cyclon powder, prepared at our laboratories at a pilot scale, was used as the active agent (1). Content of the main fatty acids as determined by GC/MS, which are favourable in cosmetic preparations (2), was reported to be (1): 4.3% myristic, 0.4% pentadecanoic, 38.3% palmitic, 0.8% margaric, 9.1% stearic, 14.1% oleic, 12.6% linoleic, 18.6% linolenic, 0.6% arachidic acids.

Following preliminary studies on formulation and investigating the consistency, satisfactory appearance and stability characteristics, 30% Texapon N 40®, 1 % active agent, 3% Comperlan KD®, 10% Dehyton G®, 2% NaCl, 0.2% methyl paraben, 0.24% citric acid and sufficient quantity of distilled water to make up 100 g, were used. Shampoo formulation was prepared by mixing at 50°C and 200 rpm for 1.5 hr. pH value was adjusted to 5.52 by the addition of citric acid.

Characterization of the Shampoo

Foam Power and Stability

Foaming property of the shampoo was determined using Ross-Miles test (3). This test provides not absolute but comparative data on the stability of foam.

Rheological Analysis

The rheological properties of the shampoo prepared was determined by a rheometer using cone-plate geometry, at constant temperature of 20±0.1°C. Speed of the cone was increased and then simultaneously decreased within a range of 10-100 rpm. Following the determination of the flow type, fit to one of the mathematical models available was investigated.

Stability Tests

Different samples of the shampoo were kept at various conditions, room temperature (25°C), refrigerator (4°C), oven (40°C) and stability cabin (40°C and 60% relative humidity) and followed subjectively every day for any change in appearance, colour, odour, texture and consistency.

Dermatological Tests

15 female volunteers were used. The ages of the volunteers were between 19 and 46. Volunteers were asked to quit using any cleansing shampoos 5 days prior to the study. After controlling the unity of the forearms of all volunteers, shampoo samples were applied undiluted to 2 cmX2 cm area. The areas were closed by sterile patches for 24 hours. Erythema was measured objectively just before and after 24 hr of application using Mexameter.

Volunteers who were uninformed about the content of the shampoo were asked to use a definite amount of the preparation, twice a week. Moisture and sebum contents of hair and scalp, respectively, were measured, in a conditioned room of 25°C and 40% relative humidity, prior to the use of shampoo and once a week for 15 days of application. Panel tests prepared previously were filled in by the volunteers independently at the end of 2 weeks.

Results and Discussion

Clear liquid shampoos, with the appropriate consistency, have become popular with the availability of synthetic detergents, which have made it possible for the shampoo to work with hard water as well as soft water, without leaving behind residue on hair. Simple formulations with minimum number of ingredients and natural fragrances are gaining popularity because of the environment friendly sentiments.

Formulation of the Shampoo

A good shampoo, besides the many attributes, must provide adequate cleansing of hair. With surfactants as the main cleansing agents of shampoos, the prime requirement is that the amount of detergent in the wash liquor must be above the critical micelle concentration-CMC (4).

Alkyl ether sulfates are milder and less irritant to eyes, compared to alkyl sulfates, and therefore sodium laureth sulfate has been used in our formulation. Presence of certain amphoteric surfactants can significantly reduce the eye irritancy of anionic surfactants. Therefore, cocoampho diacetate has been used in the formulation.

Majority of these cleaning shampoos are based on anionic surfactants in conjunction with an effective foam stabilizer. A rich and stable foam is indispensable and is still perceived as good cleaning of hair (5). Even though sodium laureth sulfate is a good foamer, the loose structure of the foam is needed to be modified to maintain the foam quality even in the presence of sebum. The foam booster, namely cocoamide diethanolamine, has been incorporated into the formulation for such concerns (6).

Natural ingredients play a big role in new shampoo launches which all promote the benefits of naturals. However, science and nature have to be combined to develop innovative products. Aloe vera and mango, citrus peach, melon rose, kiwi, peppermint, rosemary, olive, eucalyptus, almond, coconut and wheat have been used in shampoos to deliver moisturizing, body-building and protective benefits (7,8). Lipids of *Origanum* cyclon powder have been tested in this study for their efficacy when formulated in a shampoo to see the feasibility of the discarded fraction of the plant with economical concerns.

Human scalp is generally accepted to show the pH value of 5.5 even though there are some variations due to several conditions. The pH value of preparations to be applied are aimed to approximate this value. When the pH of the shampoo prepared was measured, it was found to be 7.99. Therefore, citric acid was added to the formulation to decrease the pH value to 5.52.

Fragrance plays a critical role in hair care products. However, to minimize any interferences with the plant extract and to test the odour of the 'natural' in the shampoo formulated, no fragrance has been incorporated into the formulation. Yield of the essential oils of the lipid powder was found to be 6.5% (1). Content of the essential oils was determined by GC/MS and the main components were found to be: 4.47% linalool, 1.43% terpinene-4-ol, 2.16% borneol, 9.14% thymol and 73.24% carvacrol (1).

Preservatives are required substances in shampoos to safeguard against microbial actions. Methyl paraben has been incorporated into the formulation keeping in mind its aqueous solubility and where it functions (9).

Foam Power and Stability

Foam heights measured undiluted according to Ross-Miles test were 6 mm and 4 mm. This gives a hint to good foam stability. There is an evidence that good foamers are not certainly irritant, however, most of the irritant preparations are good foamers (10). Result of nonirritancy in the sensory evaluation of the shampoo confirms this data.

Rheological Analysis of the Shampoo

Proper consistency is essential for a liquid shampoo, which should be thin enough for pouring out easily but sufficiently viscous to hold on the hand and apply to hair and scalp. A shampoo should be able to be spread evenly into the hair and rinse well without effort. For anionic shampoos, to achieve the desired viscosity, inorganic salts are added to the formulation. Sodium chloride, is believed to have the ability of increasing the swelling of surfactant micelles and can be used over a broad range of pH (11).

When tested rheologically at 20°C temperature, the shampoo formulated showed a shear thinning index of 1.02 indicating almost a Newtonian flow type. This indication can be followed in Table 1 where the shear rate-shear stress ratio demonstrates almost a linear relation. Shear thinning in-

Table 1. Rheological data of the shampoo formulated

RPM	Viscosity (mPas.sec)	Shear Stress ($Dyn.cm^{-2}$)	Shear Rate (sec^{-1})
10.0	122.9	47.2	38.4
20.0	128.0	98.3	76.8
30.0	131.4	151.4	115.2
40.0	128.0	196.6	153.6
50.0	128.0	245.8	192.0
60.0	124.6	287.0	230.4
70.0	125.1	336.2	268.8
80.0	124.2	381.4	307.2
90.0	124.0	428.6	345.6
100.0	125.4	481.7	384.0

dex shows the ratio of decrease in viscosity related to the increase in shear rate and has a value of 1 for the Newtonian flow. When the fit to various mathematical models were investigated, Bingham model with a 99.2% confidence of fit was found to be the best. According to this model, where the pseudoplastic flow obeys the equation

$$\gamma = \gamma_0 + \eta \, . \, D,$$

plastic viscosity (η) was 123.6 mPas.sec and yield stress (γ_0), *ie* the shear stress at time 0, was 4.33 D/cm^2 (12). In this equation, γ is the shear stress at time t and D is the shear rate.

Stability Testing of the Shampoo

Stability testing provides data on the performance of the preparation during ageing (13,14). The shampoo formulation kept at elevated conditions and evaluated subjectively, considering the appearance, colour, odour, texture and consistency, have not shown changes within 40 days which indicate good stability.

Dermatological Testing of the Shampoo

Panel Tests

A properly designed and conducted panel test is believed to be able to assess the degree of preference of the various shampoo attributes of the prototype. In the sensory panel testing of the shampoo prepared, monadic product test has been used which requires the respondents to use only one product. This type of test is simple to design and execute, its results can be compared over time, it is less time-consuming than other tests which require multiple product use.

Results of the sensory panel tests have been evaluated by 'ordinal scales' and given in Figure 1. These scales require the ability to rank specific attributes. Direct-judgement rating method used for ordinal scaling, where the respondent is asked to give numerical rating to each designated attribute, is easy to apply and the unit of measurement is obtained directly (15).

When evaluated at a scale range of –5 and 5, appearance, consistency and odour of the shampoo seems to be disliked by the volunteers. This is perhaps because of the unfamilarity to clear liquid shampoos without pearlescent agents. Dominant odour of carvacrol seems to be unesteemed since floral notes are generally preferred in shampoos (4). Other attributes are ranked in the positive region and especially the spreadability on hair and foaming property is worth mentioning as positive attributes.

There is a significant difference between dry and wet combabilities. Wet combability is an important criterion if no further conditioning is performed after washing (16). In our case, it can be said that wet combability can not be the only criterion since the other attributes including dry combability seems to be satisfactory.

Moisturization of the Shampoo

Percentage of increase in hair moisture upon application of the shampoo formulated is shown in Figure 2a.

Hair, absorbing or losing water, is affected by the relative humidity of the environment. It is very sensitive to changes in humidity: when the moisture content is high parallel to the humidity of air, hair body and hold is lost. On the contrary, when the level is low, hair becomes dry and brittle. It was found that the degree of relative humidity affects the diameter of hair to a great extent while the length increases slightly (17).

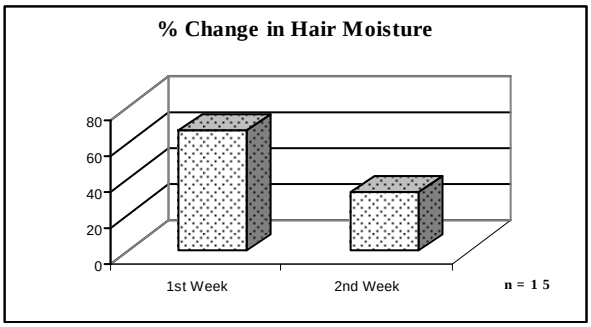
Figure 1. Results of the Sensory Panel Test (n=15).

While there is a mean increase of 66.7±188.7% at the end of the 1st week, there is an increase of 32.2±123.8% in moisture at the end of the second week. There is a high inter-individual variation as followed by the standard deviation values. This is expected due to different characteristics of hair of the volunteers. The increase in moisture content is almost the half of the first week probably owing to the adoptance to the formulation used regularly.

Reoiling of the Shampoo

Even though hair fiber is relatively hydrophilic, hair sebum, aged for even a day or two, is typically a viscous waxy material. Hair picks up sebum continuously from the scalp to reoil the hair, and thus hair slowly becomes oily again following shampooing. Hair reoiling mostly is related to the nature of the surfactants used to wash hair (4). The accumulation of sebum on hair is believed to be the net result of sebum migration from the follicules to the hair and the sebum loss through combing (18). Both processes can be modified by a shampoo and therefore it is reasonable to investigate the reoiling of hair after shampooing.

Percentage of increase in scalp sebum after application of the shampoo formulated is shown in Figure 2b. The mean increase in scalp sebum following the first and second weeks were determined to be 112.8±158.4 and 34.5±121.8, respectively. The inter-individual variation is present also like other properties of hair. There is again a decrease compared to the first week.



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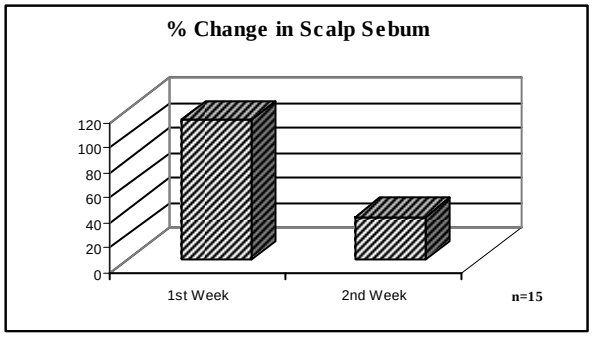

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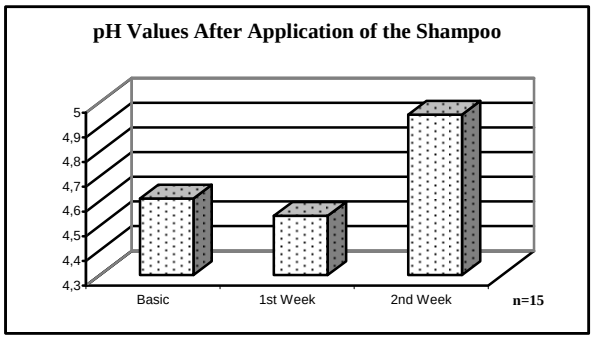

c

Figure 2. Variations in Moisture, Sebum and pH After Application of the Shampoo Formulated.

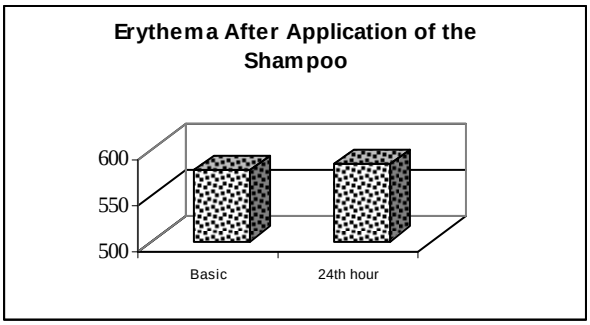

Figure 3. Erythema Values Determined in the Patch Test.

Skin pH Values

Shampoo formulated have not shown dramatic changes in scalp pH maybe due to the accordance of shampoo pH with the scalp pH. pH values of the scalp (Figure 2c) determined before and after 1 and 2 weeks of application were 4.6±0.2, 4.5±0.1 and 4.9±0.2, respectively. While only one volunteer had a pH of 5.0 before application, pH value of 5 or over have been determined in 9 volunteers at the end of the second week. This gives a hint to the effect of the shampoo with a pH of 5.52.

Irritation Potential of the Shampoo

Patch test is adequate to determine any irritation or sensitization potential of a cosmetic preparation (19). The classical sign of inflammation, erythema has been measured (Figure 3) and no significant variation ($p>0.05$) could be determined at the end of the 24^{th} hour. Basic erythema value was 577.5±15.9 while it was 583.4±14.4 after 24 hours. This is in accordance with the results of the sensory panel test where no irritancy has been declared.

Conclusion

The shampoo formulated seems to meet the expectations in terms of usage convenience and functional efficacy. Aesthetics of the product is not satisfactory and needs to be modified.

Lipid extract of *Origanum* cyclon powder obtained at a pilot scale and which is regarded as discard material can be used cosmetically because of its high content of fatty acids. This material is worth further studying, especially in skin care preparations.

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