Journal of Biomedical and Pharmaceutical Research
Available Online at www.jbpr.in
CODEN: - JBPRAU (Source: - American Chemical Society)
NLM (National Library of Medicine): ID: (101671502)
Index Copernicus Value 2024: 84.28
Volume 15, Issue 3; 2026, 1-6

ISSN (Online): 2279-0594
ISSN (Print): 2589-8752

Review Article

Formulation and Factorial Optimization of a Sulfate-Free Polyherbal Anti-Dandruff Shampoo Employing Plant-Derived Saponins

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Article Info: Received: 11-03-2026 / Revised: 04-04-2026 / Accepted: 27-04-2026
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DOI: https://doi.org/10.32553/jbpr.v15i5.1450
Conflict of interest statement: No conflict of interest

Abstract:
Conventional anti-dandruff shampoos are predominantly based on anionic sulfates such as sodium lauryl sulfate, which provide strong detergency and foam but can disrupt the scalp barrier, increase transepidermal water loss and aggravate irritation during long-term use. In contrast, consumer demand is shifting toward herbal, sulfate-free products that offer milder cleansing and improved biocompatibility without compromising performance. In response to this need, the present investigation proposes a sulfate-free polyherbal anti-dandruff shampoo in which plant-derived saponins from Sapindus mukorossi (Reetha) and Acacia concinna (Shikakai) function as true biosurfactants, providing cleansing and foaming while helping maintain scalp pH. The formulation further integrates tea tree oil, neem and tulsi extracts as antifungal and anti-inflammatory agents, and uses xanthan–guar gum as a natural rheology system to achieve acceptable viscosity, shear-thinning behaviour and conditioning feel. A structured formulation strategy employing factorial design will be used to optimize the ratio of saponins and gums, followed by comprehensive evaluation including pH, viscosity, surface tension, foam characteristics, cleansing efficiency, protein denaturation, and comparison with a marketed sulfate-based shampoo. Accelerated stability studies at elevated temperature and humidity will assess physical and functional robustness.
Keywords: Sulfate-free polyherbal anti-dandruff shampoo; Sapindus mukorossi; Acacia concinna; Tea tree oil; Neem; Tulsi; Plant saponins; Biosurfactant-based cleansing; Xanthan–guar gum; Malassezia dandruff.

Introduction

Sulfate-Free Polyherbal Shampoo: Hair cleansing is one of the oldest personal care practices, but the chemistry behind shampoos has changed dramatically from traditional botanical washes to modern synthetic surfactant systems. Conventional shampoos rely largely on anionic sulfates such as sodium lauryl sulfate (SLS) and sodium lauryl ether sulfate (SLES), which provide strong detergency and abundant foam but are increasingly criticized for scalp irritation, barrier disruption, and environmental impact. In parallel, there is a visible consumer

shift toward herbal and "clean label" formulations that promise milder action, better biocompatibility, and sustainability. [1]

Herbal shampoos available in the market, however, often retain SLS or similar synthetic detergents as the primary cleansing agent, while the plant components are used merely as marketing additives rather than functional surfactants. This creates a gap between consumer expectations of safety and naturalness and the actual formulation architecture.

A sulfate-free polyherbal shampoo built on genuine biosurfactants particularly plant saponins from Sapindus mukorossi (Reetha) and Acacia concinna (Shikakai) offers a scientifically coherent path to bridge this gap by replacing harsh synthetic surfactants with natural saponin systems that can cleanse, foam, and contribute antifungal activity simultaneously. [2]

The polyherbal concept further integrates antifungal and anti-inflammatory actives such as Melaleuca alternifolia (Tea tree oil), Azadirachta indica (Neem), and Ocimum sanctum (Tulsi), along with natural rheology modifiers like xanthan and guar gum, to design a sulfate-free shampoo with targeted anti-dandruff action, pleasant sensory profile, and acceptable quality attributes comparable to marketed products. Within this broader context, the present work positions sulfate-free polyherbal anti-dandruff shampoo as an evidence-based advance at the interface of ethnopharmacology and modern cosmetic science. [3]

Need for this study

Despite the rapid growth of herbal and anti-dandruff shampoo segments, most commercial formulations still depend on SLS or related sulfates as the core detergent. SLS is known to increase transepidermal water loss, elevate scalp surface pH, denature keratin, and induce features of irritant dermatitis on repeated use, which is particularly problematic for chronic conditions like dandruff that require long-term, frequent cleansing. This creates a therapeutic paradox: the surfactant base itself can aggravate barrier dysfunction and Malassezia proliferation, undermining the action of the antifungal active it is supposed to deliver. [4]

At the same time, epidemiological data highlight dandruff and seborrheic dermatitis as highly prevalent, chronic, and recurrent disorders associated with Malassezia yeasts, altered sebum, and impaired scalp barrier, with substantial psychosocial and economic burden. There is a clear need for anti-dandruff shampoos that are safe enough for continuous long-term use, minimize scalp irritation, and preferably support restoration of the acid mantle rather than disrupt it. Plant-based biosurfactant systems using Reetha and Shikakai as true functional cleansers offer such a possibility but are still under-optimized and under-represented in rigorously designed formulations.

Moreover, existing herbal shampoos often lack systematic formulation optimization, robust physicochemical evaluation, and comparative data versus sulfate-based benchmarks. A study that deliberately constructs a 100% naturally derived surfactant base, integrates clinically supported herbal antifungal actives like Tea tree oil, and applies design of experiments (DoE) to optimize foaming, viscosity, and cleaning performance addresses a genuine scientific and industrial gap. The present investigation therefore responds both to consumer-driven demand and to an unmet technical need for sulfate-free, evidence-based polyherbal anti-dandruff systems. [5]

Key features of this study: This study is characterized by several distinctive features that differentiate it from generic herbal shampoo formulations:

1. **Use of a fully biosurfactant base**

Reetha and Shikakai saponins are employed as the primary and secondary surfactant system, respectively, eliminating SLS and similar synthetic detergents and allowing cleansing and foam generation to be mediated entirely by natural saponins.

2. **Rational ratio of saponin components**

A 3:1 Reetha:Shikakai saponin complex is chosen to exploit complementary functions Reetha providing strong foaming and cleansing with documented antifungal effects, and Shikakai contributing mild cleansing, natural acidic pH (4.5–5.5), and tannin-mediated cuticle conditioning. [6]

3. **Targeted anti-dandruff phytotherapy**

Tea tree oil standardized to terpinen-4-ol is incorporated as the primary antifungal active against Malassezia, supported by Neem and Tulsi extracts with additional antifungal, anti-inflammatory, and immunomodulatory effects. This multi-herb combination aims to address both fungal load and scalp inflammation.

4. **Natural rheology and sensory optimization**

Xanthan and guar gum are combined in a synergistic 0.5% + 0.5% system to achieve desirable viscosity, shear-thinning behavior, and slip comparable to synthetic polymer thickeners, while maintaining a "natural" excipient profile.

5. **Systematic experimental design and benchmarking**

Multiple trial batches are developed under factorial design to optimize concentrations of the saponin complex and gum blend, followed by extensive physicochemical evaluation (pH, viscosity, surface tension, foam index, cleaning action) and comparison with a marketed sulfate-based shampoo, including protein denaturation tests and accelerated stability studies. [7]

Together, these features position the formulation not merely as a herbal cosmetic, but as a rigorously developed sulfate-free polyherbal system with potential for real-world translation.

Mechanism of action of sulfate-free polyherbal anti-dandruff shampoo

The mechanism of action of the proposed sulfate-free polyherbal shampoo is multi-layered, involving biosurfactant-mediated cleansing, targeted antifungal effects, scalp barrier protection, and anti-inflammatory activity.

Biosurfactant cleansing and foaming

Saponins from Sapindus mukorossi and Acacia concinna are amphiphilic glycosides composed of a lipophilic triterpenoid aglycone and hydrophilic sugar chains, enabling them to behave as natural surfactants. In aqueous solution, these molecules reduce surface tension and form micelles above the critical micellar concentration, solubilizing sebum lipids, particulate dirt, and cosmetic residues within their hydrophobic core. Mechanical agitation during shampooing introduces air, and the saponins stabilize foam bubbles by rapidly adsorbing at the air-water interface, creating the characteristic lather associated with cleansing.

Unlike negatively charged sulfates, saponins are largely nonionic and thus do not interact strongly with the negatively charged keratin of the hair cuticle, minimizing protein denaturation and cuticle lifting. As a result, they can remove surface contaminants effectively while better preserving cuticle architecture, tensile strength, and shine compared with SLS-based systems. [8]

Maintenance of scalp acid mantle and barrier

The scalp's hydrolipidic film naturally maintains a mildly acidic pH of around 4.5–5.5, which supports barrier integrity, commensal microflora, and controlled activity of fungal lipases. Shikakai extracts possess an intrinsic pH in this acidic range due to organic acids such as tartaric and ascorbic acid and act as a natural buffer when incorporated into the shampoo base.

This allows the final formulation to remain within the physiological pH window without heavy reliance on synthetic acidulants, thereby preserving acid mantle and minimizing cuticle swelling and barrier disruption.

By contrast, SLS-based formulations tend to increase scalp surface pH, which can enhance Malassezia lipase activity, promote barrier leakiness, and accelerate corneocyte shedding,

all of which favor dandruff pathophysiology. The sulfate-free polyherbal formulation therefore aims to reverse this pattern by using mildly acidic, non-denaturing biosurfactants aligned with the scalp's natural environment. [9]

Antifungal and anti-inflammatory effects

Tea tree oil (TTO), standardized under ISO 4730, is rich in terpinen-4-ol, which exerts potent antifungal action through insertion into fungal membranes, increasing membrane fluidity and permeability, causing leakage of intracellular constituents, dissipation of proton gradients, and eventual fungal cell death. This mechanism operates independently of ergosterol synthesis and thus remains effective against azole-resistant Malassezia strains. In addition, terpinen-4-ol has been shown to suppress pro-inflammatory cytokines such as TNF-α and IL-1β, providing symptomatic relief from pruritus and scalp inflammation associated with dandruff.

Reetha saponins themselves show antifungal activity against dermatophytes and yeasts, acting as membrane-active agents that disrupt fungal cell envelopes and complement the effect of Tea tree oil. Neem and Tulsi supply further antifungal and anti-inflammatory phytoconstituents, creating a polyherbal network of activities targeting Malassezia load, sebum dysregulation, and local immune responses. The combined effect is expected to reduce fungal biomass and lipid-mediated irritant metabolites on the scalp while calming inflammatory cascades that drive excessive keratinocyte turnover. [10]

Rheology, deposition, and conditioning

The xanthan guar gum system confers pseudoplastic, shear-thinning behavior: viscosity decreases under shear during pouring and massage, then recovers when shear stops, allowing the shampoo to stay on the scalp long enough for actives to act. Guar, as a cationic-deposition-friendly galactomannan, can form a thin film on the hair surface, improving lubricity, wet combability, and overall feel, while xanthan contributes to viscosity and suspension stability of dispersed herbal particles. This rheological profile not only enhances sensorial quality but may also support more uniform distribution and short-contact-time deposition of Tea tree oil and other actives on the scalp surface.

Applications of sulfate-free polyherbal shampoo

The primary application of sulfate-free polyherbal shampoo is in the long-term management of dandruff and mild seborrheic dermatitis of the scalp. Its design aims to make daily or frequent use feasible without the barrier damage, irritation, or excessive dryness often associated with conventional anti-dandruff shampoos.

Beyond dandruff, such formulations can be useful for individuals with:

1. Sensitive or irritation-prone scalps that react to sulfates or strong synthetic preservatives.
2. Chemically treated or damaged hair, where minimizing cuticle disruption and protein loss is crucial to maintain strength and shine.
3. Preference for natural, eco-friendly personal care products, as plant-derived saponins and gums are biodegradable and less likely to contribute to aquatic toxicity than some synthetic surfactants and preservatives.

Sulfate-free polyherbal shampoos also hold potential as base platforms for further customization for example, integrating additional actives for hair fall control, color protection, or scalp psoriasis management while maintaining an SLS-free, herbal-centric excipient structure. [11]

Limitations of sulfate-free polyherbal shampoos

Despite their advantages, sulfate-free polyherbal shampoos present certain limitations that must be acknowledged and systematically addressed. First, plant saponins and essential oils can show batch-to-batch variability in composition and potency due to differences in plant source, harvesting conditions, and extraction methods, necessitating robust standardization strategies

(e.g., quantification of total saponins, terpinen-4-ol content). Without such controls, consistency of cleansing, foaming, and antifungal efficacy may be compromised. Second, biosurfactant systems may initially exhibit lower foam volume or different foam texture compared with SLS shampoos, which can be perceived by consumers as "less effective", even when objective cleaning performance is adequate. Sensory optimization (viscosity, fragrance, foam feel) and consumer education are therefore important to ensure acceptance.

Third, the stability of complex polyherbal systems combining multiple extracts, gums, and volatile oils can be challenging, with risks of viscosity drift, phase separation, or fragrance loss during storage, especially under elevated temperature and humidity. Accelerated stability testing as per ICH-adapted conditions is required to define shelf life and packaging needs.

Finally, while in vitro and short-term in vivo data support the safety and efficacy of key herbal actives, large, well-controlled clinical trials comparing sulfate-free polyherbal shampoos directly with standard anti-dandruff agents remain limited, so claims must be framed cautiously until such data accumulate. [12]

Formulation and evaluation

The formulation of the sulfate-free polyherbal anti-dandruff shampoo follows a cold-process approach to protect thermolabile saponins, polyphenols, and volatile essential oil constituents. In a typical batch, standardized aqueous extracts of Reetha and Shikakai are combined in a 3:1 ratio, hydrated xanthan–guar gum blend (0.5% + 0.5%) is dispersed to achieve the desired rheology, and Tea tree oil is pre-solubilized with polysorbate 80 (5:1 ratio) before incorporation into the aqueous base alongside Neem, Tulsi, Aloe vera, preservatives, fragrance, and pH adjusters.

Physicochemical evaluation includes:

1. Appearance and odor (clarity, color, absence of phase separation, hedonic odor scoring).
2. pH of a 10% shampoo solution, targeting 4.5–5.5 to match scalp acid mantle.
3. Viscosity measurement using a Brookfield viscometer to ensure acceptable pourability and sensory feel (typically 2000–4000 cP).
4. Surface tension (Stalagmometer/tensiometer), aiming for reduction from 72 dyn/cm (water) to ≤40 dyn/cm as a marker of adequate surfactant performance.
5. Foam volume and stability by cylinder-shake method, evaluating initial foam height and foam persistence after 5 minutes.
6. Wetting time of a canvas disc and dirt dispersion tests to assess cleansing efficiency and anti-redeposition behavior.

Performance and safety testing further include in-vitro protein denaturation or keratin degradation assays as indicators of scalp-friendliness, as well as comparative cleaning efficiency and protein denaturation versus a marketed SLS-based anti-dandruff shampoo. Accelerated stability studies at 40 ± 2 °C / 75 ± 5% RH for three months examine the robustness of the optimized formulation with respect to appearance, pH, viscosity, foaming, and microbial integrity. [13]

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