Standardized Styrax benzoin Resin Nanoemulsion: A Novel Chitosan-Coated Phytocosmeceutical Delivery System

Program Riset PRIMA ITB 2026 — Skema Riset: Riset Unggulan ITB

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ABSTRACT

Commercial grading of *Styrax benzoin* resin lacks scientific phytochemical standardization, limiting its deployment in topical delivery systems. This study standardized three commercial resin grades (A, B, C) via LC-HRMS/MS, TLC-densitometry, and colorimetric assays, subsequently developing an optimized chitosan-coated nanoemulsion (CNE) using the verified premium extract. Premium Grade A demonstrated significant phytochemical and biological superiority, yielding the highest free trans-cinnamic acid content (31.18% w/w), total phenolics (153.38 mg GAE/g), total tannins (77.04 mg TAE/g), DPPH scavenging (IC_{50} 19.70 ppm), and astringent capacity (313.63 mg TAE/g). Interfacial coating with 0.1% w/v chitosan (CNE 0.1%) produced an optimal core-shell monolayer shield (droplet size 31.43 nm, PDI 0.49, encapsulation efficiency 57.59%) confirmed by TEM and ATR-FTIR, whereas 0.3% chitosan induced bridging flocculation. Under 6 accelerated thermal stress cycles (4°C/40°C), CNE 0.1% displayed contractive kinetic stability, with droplet dimensions stabilizing at 25.63 nm (PDI 0.37). Integrating raw material standardization with interfacial engineering establishes a thermodynamically resilient core-shell nanoemulsion for topical anti-acne phytocosmeceuticals. The optimized CNE 0.1% demonstrates promising potential as a stable nanocarrier for topical anti-acne delivery.

Keyword: *Styrax benzoin*, Chitosan Coating, Interfacial Engineering, Core-Shell Nanoemulsion, Phytocosmeceuticals

INTRODUCTION

Management of dermatological conditions such as acne vulgaris associated with Cutibacterium acnes, Staphylococcus aureus, and Staphylococcus epidermidis increasingly relies on natural biopolymers and botanical cosmeceuticals. Sumatran benzoin resin (Styrax benzoin) is rich in bioactive cinnamic acids, phenolics, and tannins, offering potent antioxidant, astringent, and antimicrobial properties. However, commercial sorting (Grades A, B, and C) depends solely on visual appearance and bark debris without scientific substantiation. Furthermore, the highly viscous, resinous, and lipophilic nature of raw S. benzoin severely restricts its aqueous dispersibility and topical skin bioavailability.

Nanoemulsion carriers enhance the dispersion and thermodynamic stability of hydrophobic phytochemicals. Interfacial deposition of cationic chitosan biopolymer provides robust electrostatic and steric stabilization against droplet coalescence and Ostwald ripening. This study aimed to: (1) scientifically validate the phytochemical profiles and in vitro bioactivities of commercial S. benzoin grades; and (2) engineer an optimized core-shell chitosan-coated nanoemulsion (CNE) delivery system using the validated premium extract for topical dermatological applications.

RESEARCH METHODS

Resin Extraction & Standardization: Raw resin granules (Grades A, B, C) were extracted via Soxhlet extraction using 96% ethanol. Grade A metabolites were mapped via UHPLC-HRMS/MS. Free *trans*-cinnamic acid was quantified using TLC-densitometry (254 nm), while TPC and TTC were measured colorimetrically.

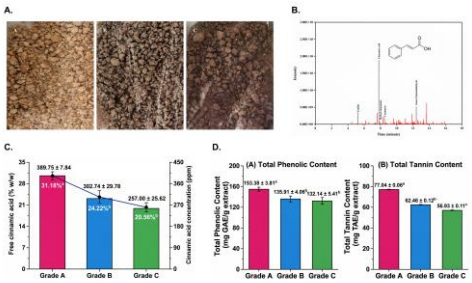
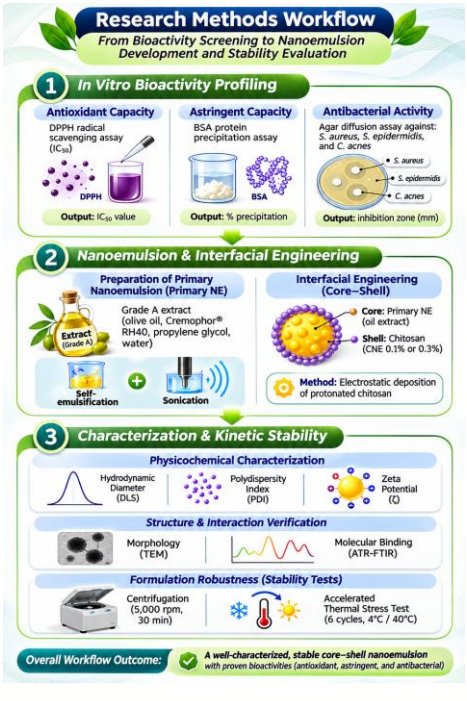


Figure 1. Raw material grading and phytochemical standardization. (A) Simplisia comparison; (B) LC-HRMS chromatogram; (C) Free cinnamic acid content; (D) TPC and TTC profiles.



DISCUSSION & RESULTS

Raw Material Quality Validation: Grade A demonstrated statistically significant phytochemical superiority ($p < 0.05$) over Grades B and C. Grade A yielded the highest free *trans*-cinnamic acid (31.18% w/w; 389.75 ppm), TPC (153.38 mg GAE/g), and TTC (77.04 mg TAE/g). This directly governed its bioactivity, exhibiting superior DPPH radical scavenging (IC_{50} 19.70 ppm; "very potent"), protein-precipitating astringency (313.63 mg TAE/g), and antibacterial inhibition against *S. aureus*, *S. epidermidis*, and *C. acnes*.

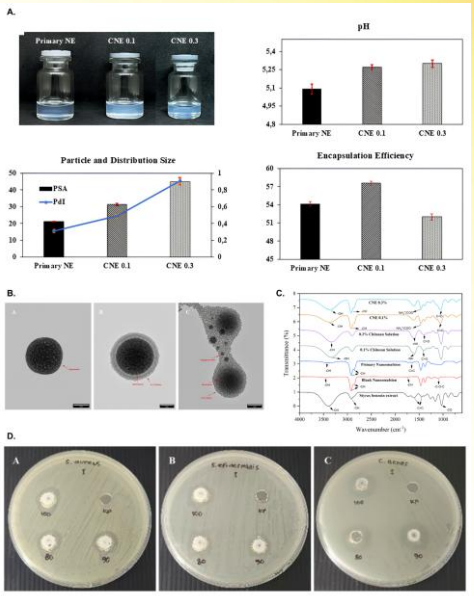


Figure 2. Characterization of chitosan-coated nanoemulsions (CNE). (A) Physicochemical & DLS properties; (B) TEM morphology; (C) ATR-FTIR spectra; (D) In vitro antibacterial activity.

Interfacial Engineering & Optimization: Deposition of 0.1% w/v chitosan (CNE 0.1%) expanded hydrodynamic droplet size from 21.20 nm (Primary NE) to 31.43 nm with narrow polydispersity (PDI 0.49) and peak encapsulation efficiency (57.59%). Conversely, 0.3% chitosan induced polymer chain overcrowding and bridging flocculation, causing size enlargement (44.53 nm) and severe PDI broadening (0.89).

Morphological & Molecular Proof: TEM micrographs confirmed a discrete, uniform core-shell monolayer "halo" surrounding CNE 0.1% nanospheres. ATR-FTIR spectra demonstrated interfacial surface masking at 1560 cm^{-1} ($-NH_3^+/COO^-$), validating complete outer biopolymer encapsulation over the lipid core.

Thermodynamic Kinetic Stability: Across 6 thermal shock cycles (4°C/40°C), CNE 0.1% exhibited contractive thermodynamic relaxation, with droplet dimensions stabilizing at 25.63 nm (PDI 0.37). In contrast, uncoated Primary NE suffered Ostwald ripening coarsening (size expanded from 21.20 nm to 30.03 nm, PDI 0.48).

CONCLUSIONS

