

MRS Advances © 2018 Materials Research Society
DOI: 10.1557/adv.2018.619



Synthesis of Eco-friendly Nano-Structured Biosurfactants from Vegetable Oil Sources and Characterization of Their Interfacial Properties for Cosmetic Applications

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ABSTRACT

In this study, 3 types of zwitterionic phospholipid biosurfactants LDP(S), CDP(S) and CTD(P) were prepared from 3 different raw materials such as rapeseed oil, coconut oil and cottonseed oil respectively. The structure of the resulting phospholipid biosurfactants was elucidated by FT-IR, ^1H NMR and ^{13}C NMR spectroscopies and their interfacial properties have been examined such as CMC, static surface tension, wetting property, solution stability, and foam property. Interfacial property measurement and prescription test in cosmetic formulation prepared with the newly synthesized biosurfactants revealed that CDP(S) biosurfactant possesses excellent mildness and superior interfacial properties, indicating the potential applicability in cosmetic product formulations.

INTRODUCTION

The enormous market demand for surfactants is currently met by numerous synthetic, mainly petroleum-based, chemical surfactants [1]. These compounds are usually toxic, non-biodegradable and environmentally hazardous. Tightening environmental regulations and increasing awareness for the need to protect the ecosystem have effectively resulted in an increasing interest in biosurfactants as possible alternatives to chemical surfactants [1].

Biosurfactants can be defined as the surface-active biomolecules produced by microorganisms with wide-range of applications. They have advantages over their chemical counterparts in specificity, relative ease of preparation, mildness, and effectiveness even at extreme temperature or pH. Biosurfactants also have the merit of diversity, environment friendly nature such as nontoxicity and excellent biodegradability,

possibility of large-scale production, selectivity, performance under extreme conditions, and potential applications in environmental protection [1]. Due to their unique functional properties, biosurfactants have been used in various industries including agriculture, fertilizers, petroleum, petrochemicals, cosmetics, pharmaceuticals, personal care products, food processing, beverages, textile manufacturing, metal treatment and processing, pulp and paper processing, paint industries and many others [1]. They can be used as emulsifiers as well as demulsifiers, wetting agents, foaming agents, spreading agents, environmental cleanup of pollutants, functional food ingredients and detergents [1].

In this work, environmentally friendly zwitterionic phospholipid biosurfactants were synthesized using 3 different sources such as rapeseed oil, coconut oil, and cottonseed oil respectively. Of particular interest in this study was to compare interfacial properties of 3 types of phospholipid biosurfactants synthesized from rapeseed oil, coconut oil, and cottonseed oil respectively and investigate their potential applicability in cosmetic product formulations.

EXPERIMENTAL DETAILS

Rapeseed oil, coconut oil and cottonseed oil, raw materials used in the synthesis of 3 types of phospholipid biosurfactants, were purchased from LG Household & Health Care Ltd, Korea and used without any further purification. All other reagents used for the synthesis of biosurfactants were purchased from Sigma-Aldrich Co and used as received. Water used for sample preparation was ultrapure having been double distilled and passed through a Nanopure (Sybron-Brinkman Inc.) ion exchange system.

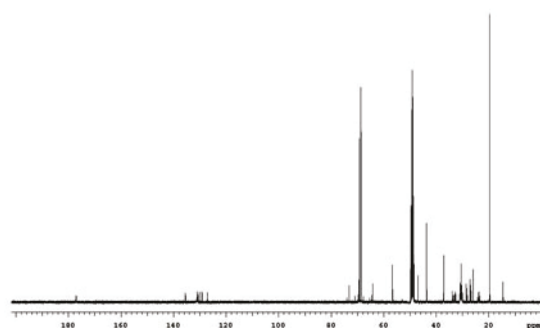
In order to determine the structure of the synthesized products, ^1H -NMR and ^{13}C -NMR spectra were recorded on a Bruker DPX 300 (300MHz) and expressed as δ units at room temperature in CDCl_3 . Digilab's FT-IR FTS-165 FT-IR spectrometer was used to obtain IR spectra of the products. The pH of surfactant was measured using a pH meter (S220-K, Mettler Toledo, USA) and the zeta potential of 1.0 wt% of aqueous surfactant solution was measured at 25°C as a function of pH by using a zeta potential analyzer (Otsuka ELS-800, Japan).

Surface tension measurements were made using a Du Nuoy ring tensiometer with a platinum ring (Kruss K100, Germany). Drop shape analysis system (Kruss DSA100, Germany) was used to measure contact angle by forming a drop of surfactant solution on a glass micro slide. A foam test apparatus (IFAC FoamScan, Germany) was used for foam stability measurement. In this study, foam stability was determined by measuring foam volume decrease during initial 1500 sec. The stability of aqueous surfactant solutions was determined by conductometric measurement (DualConTM III, ITC). The softening effect of shampoo product was evaluated by a scrubbing test and the detailed information on experimental procedure has been described in a previous study [2].

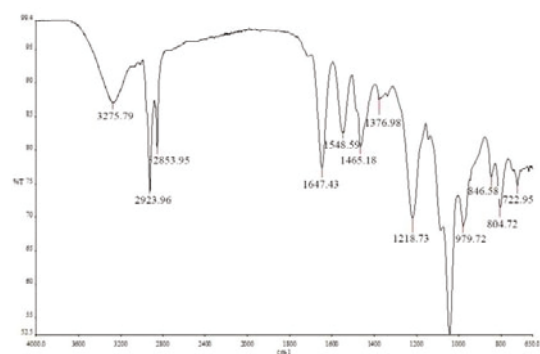
DISCUSSION

Synthesis

Synthetic route of linoleicamidopropyl (sulfur) (LDP(S)), cocamidopropyl (sulfur) (CDP(S)) and cottonseedamidopropyl (sulfur) (CTDP-W(S)) has been shown in Scheme 1 where R corresponds to rapeseed oil, coconut oil and cottonseed oil respectively. The mixture containing 1 mol of dimethylaminopropylamine and 3.2 mol of

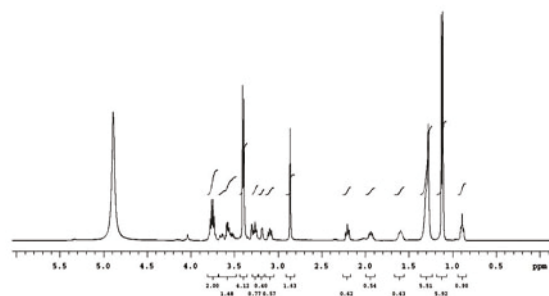


(b)



(c)

Figure 1. Spectral data of LDP(S) ; (a) ^1H -NMR spectrum in CDCl_3 , (b) ^{13}C -NMR spectrum in CDCl_3 , (c) FT-IR spectrum.



(a)

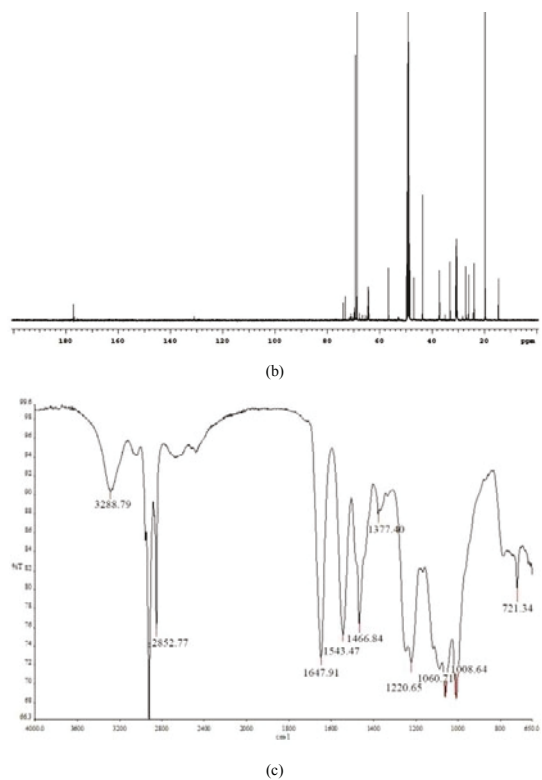
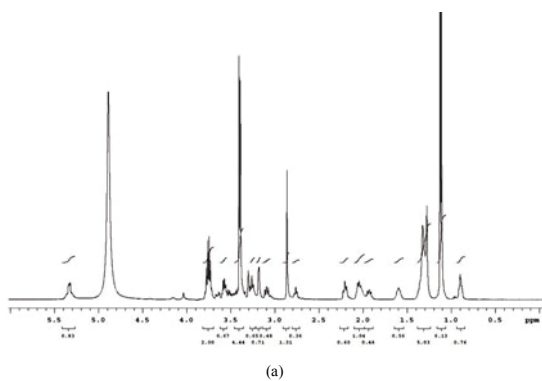


Figure 2. Spectral data of CDP(S) ; (a) ^1H -NMR spectrum in CDCl_3 , (b) ^{13}C -NMR spectrum in CDCl_3 , (c) FT-IR spectrum.



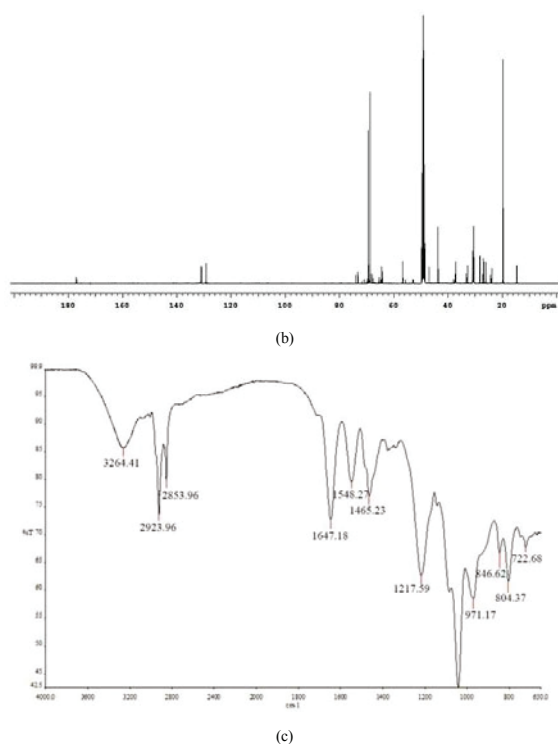


Figure 3. Spectral data of CTD(S) ; (a) ^1H -NMR spectrum in CDCl_3 , (b) ^{13}C -NMR spectrum in CDCl_3 , (c) FT-IR spectrum.

Interfacial properties

The isoelectric points of LDP(S), CDP(S) and CTD(S) surfactant systems were found to be 4.8, 8.8 and 5.2 respectively. As shown in Table 1, the pH of synthesized biosurfactants was measured using a pH meter and found to be 9.3, 5.5 and 6.3 respectively and molecular weights of LDP(S), CDP(S) and CTD(S) were 989, 801 and 896 respectively. The interfacial properties of newly synthesized biosurfactants were also measured at 25°C such as critical micelle concentration (CMC), surface tension, contact angle, foam stability and solution stability and the results are summarized in Table 1. As shown in Table 1, the CMC in mol/L of LDP(S), CDP(S) and CTD(S) surfactants are 2.41×10^{-5} , 1.20×10^{-5} and 2.58×10^{-5} respectively. Also seen from Table 1, the surface tensions of LDP(S), CDP(S) and CTD(S) surfactant systems at CMC condition are 33.61 mN/m, 31.82 mN/m and 33.37 mN/m respectively. This result indicates that CDP(S) surfactant is more hydrophobic and surface active than LDP(S) and CTD(S). As summarized in Table 1, the contact angles of LDP(S),

CDP(S) and CTDP-W(S) surfactant systems are 31.93°, 37.43° and 31.27° respectively, also indicating that CDP(S) is more hydrophobic than LDP(S) and CTDP-W(S).

In this study, the foam stability of 1 wt% surfactant solution was studied at 25°C by measuring the percentage of foam volume decrease during 1500 sec. As seen in Table 1, the percentages of foam volume decrease in LDP(S), CDP(S) and CTDP-W(S) surfactant systems correspond to 5.85, 4.72 and 5.89 respectively, indicating all the surfactants are excellent foam stabilizers. Even though the difference is not that large, more stable foams were observed with CDP(S) surfactant system. It is noteworthy that this result is consistent with that of surface tension measurement where CDP(S) exhibited a lower surface tension value than LDP(S) and CTDP-W(S). The stability of 5 wt% aqueous surfactant solution was evaluated at 25°C by measuring the electrical conductivities of top and bottom portions of a sample bottle of a surfactant solution. As shown in the Table 1, aqueous solutions of LDP(S), CDP(S) and CTDP-W(S) surfactants are considered to be stable since the difference between 2 conductivity values of top and bottom portions is relatively small.

Table 1. Summary of Physical Properties of Phospholipid Surfactants Measured at 25°C.

	MW	pH	CMC (mol/L)	Surface Tension (mN/m)	Contact Angle (°)	Foam Stability (%)	Solution Stability (1/V)	
							Top	Bottom
LDP (S)	989	9.3	2.41 x10 ⁻⁵	33.61	31.93	5.85	1.09	1.09
CDP (S)	801	5.5	1.20 x10 ⁻⁵	31.82	37.43	4.72	1.08	1.07
CTDP-W(S)	896	6.3	2.58 x10 ⁻⁵	33.37	31.27	5.89	1.01	1.03

Performance test

The test sample in shampoo formulation was prepared using 25% of Micolin A526, 30% of Micolin EA525, 5% of newly synthesized biosurfactant, 1% of FEA3, 0.5% of Tego care 450, and 38.5% of water on a weight basis. Sensory test items such as smoothness after drying, moistness after drying, foam speed, foam volume and softness were evaluated with newly synthesized biosurfactants and compared with those prepared with Mitain-CA, conventional zwitterionic surfactant used in shampoo formulation. As shown in Figure 4, CDP(S) has shown soft sensory feeling, excellent foaming ability and outstanding foam stability compared with LDP(S), CTDP(S) and Mitain-CA. A patch test has been performed with 0.1 mL of 0.5 wt% surfactant solution and the result has shown that CDP(S) indicated no allergic inflammation on a skin during 48 hrs.

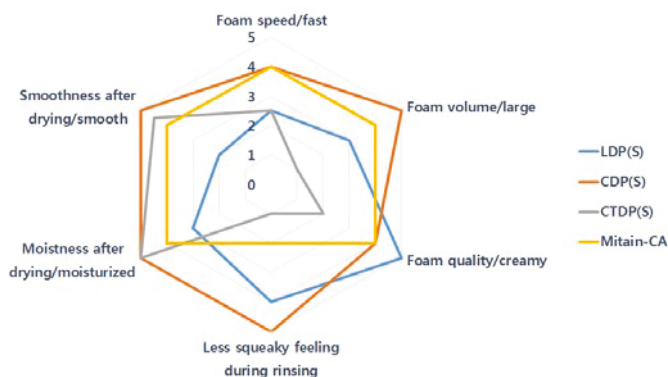


Figure 4. Prescription test result in shampoo formulation prepared with the newly synthesized biosurfactants.

CONCLUSIONS

In this study, 3 types of zwitterionic phospholipid biosurfactants were prepared using 3 different raw materials such as rapeseed oil, coconut oil, and cottonseed oil respectively and the structure of the resulting products was elucidated by FT-IR, ^1H NMR, and ^{13}C NMR spectroscopies. Interfacial property measurement indicated that all of the synthesized surfactant systems have excellent interfacial properties. In particular, CDP(S) has better interfacial properties than others such as low CMC, surface tension, excellent foam stability, and superior stability of aqueous surfactant solution. The prescription test in cosmetic formulation prepared with the newly synthesized biosurfactants indicated excellent sensory feeling and foam ability compared with conventional hydrocarbon surfactants. In particular, CDP(S) surfactant can be considered as a strong candidate for the potential applicability in cosmetic product formulations since newly synthesized CDP(S) surfactant is surface active, mild, and readily biodegradable.

ACKNOWLEDGMENTS

This work was supported by "the Global Tech Company Nurturing Program" (N063600016, Development of eco-friendly multifunctional polymer surfactant with preservative function and next generation polymer surfactant for construction) funded by the Ministry of Trade, Industry & Energy, Korea.

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