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Stability and *in Vivo* UV-Protecting Efficacy of Emulsions Stabilized with Cinnamoyl Surfactants

Seok Ho Park, Kyeongnan Kwon and Jin-Chul Kim†

Department of Medical Biomaterials Engineering, College of Biomedical Science and Institute of Bioscience and Biotechnology, Kangwon National University, 1, Gangwondaehak-gil, Chuncheon-si, Gangwon-do, 24341, Korea
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Abstract – Oil-in-water emulsion was prepared using cinnamoyl surfactants as emulsifiers. Cinnamoyl surfactants used in the present study were polyoxyethylene (20) sorbitan monolaurate-cinnamic acid conjugate (TW20CA), polyoxyethylene (20) cetyl ether-cinnamic acid conjugate (CE20CA), and polyoxyethylene(20) oleyl ether-cinnamic acid conjugate (OE20CA). The emulsion stabilized with TW20CA was the most stable, possibly because the polyoxyethylene segment of TW20CA would sterically stabilize the oil droplets effectively. *In vivo* UV protecting efficacy of surfactant and emulsion was investigated by determining the minimum amount of UV light (MAUL) to induce a black point on the back of hairless mice (HRM2). The mean MAUL of PARSOL, OE20CA, and emulsion stabilized with TW20CA was 1046.5 mJ/cm^2, 1163 mJ/cm^2, and 1308.5 mJ/cm^2, respectively. The high UV-protecting efficacy of the emulsion could be ascribed to not only the UV-absorbing property of cinnamoyl group but also the UV-scattering property of the oil droplets.

Key words: Cinnamoyl Surfactant, Emulsifier, Droplet Stability, Emulsion, *In Vivo* UV Protecting Efficacy

1. Introduction

UV-protective agents have been of great interest to the cosmetic industry, because the skin can be tanned, aged and even biologically damaged by UV light [1-4]. They can protect the skin against UV light by absorbing or scattering the light. Particles of inorganic oxide including zinc oxide, titanium dioxide, iron oxide, and magnesium oxide can reflect or scatter UV light [5-10], and they exhibit a relatively low photo-irritation because they physically block the penetration of UV into skin [11]. However, they are poorly adhesive to skin and white turbidity appears on the skin because of their light-scattering property [12]. On the other hand, organic compounds including avobenzone, oxybenzone butylmethoxydibenzoyl methane (PARSOL), cinnamic acid, octyl-triazone, and octocrylene can absorb UV light and are adhesive to skin and seldom induce white turbidity [13]. However, they are often irritative to skin under the irradiation of UV light because heat can be generated by the organic UV-absorbing compounds [14]. Recently, surfactant-cinnamic acid conjugates were developed as UV-protective emulsifiers [15]. Cinnamic acid can absorb UV light whose wavelength is 200 nm to 320 nm so surfactant-cinnamic acid conjugates can be used as UV-absorbing emulsifier as long as the conjugates exhibit an adequate amphiphilic property. In this study, cinnamoyl surfactants (polyoxyethylene (20) sorbitan monolaurate/cinnamic acid conjugate (TW20CA), polyoxyethylene (20) cetyl ether/cinnamic acid conjugate (CE20CA), and polyoxyethylene (20) oleyl ether/cinnamic acid conjugate (OE20CA)) were evaluated as UV-absorbing emulsifiers by investigating their oil droplet-stabilizing ability and *in vivo* UV-protecting efficacy. The molecular structures of TW20CA, CE20CA, and OE20CA are shown in Fig. 1. Oil-in-water emulsions were prepared using the cinnamoyl surfactants as emulsifiers. The stability of emulsions was investigated for four weeks in terms of size. Polyoxyethylene (PEO) segment is known to sterically stabilize the oil droplets because it is hydrophilic and flexible, thus acting as a spring to push away approaching oil droplets [16]. Since they have different numbers of PEO segments (three for TW20CA, one for CE20CA, one for OE20CA) and they have different number of cinnamoyl groups per one molecule, the degree of

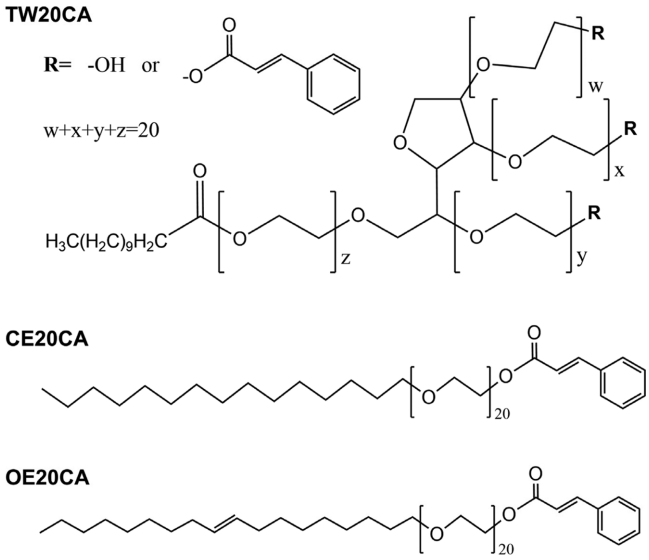

Fig. 1. Molecular structures of TW20CA, CE20CA, and OE20CA.

† To whom correspondence should be addressed.
E-mail: jinkim@kangwon.ac.kr
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freedom of POE segment, thus the stability of the oil droplet would be different depending on the kind of cinnamoyl surfactant. In addition, *in vivo* UV-protecting efficacy of a cinnamoyl surfactant (OE20CA) and an emulsion stabilized with a cinnamoyl surfactant (TW20CA) was investigated by determining the minimum amount of UV light to induce a black point on the back of hairless mice (HRM2).

2. Experimental

2-1. Materials

Butylmethoxydibenzoyl methane (PARSOL) and mineral oil were purchased from Sigma-Aldrich Co. (MO, USA). Polyoxyethylene (20) sorbitan monolaurate (TW20)/cinnamic acid (CA) conjugate (TW20CA, Tween 20/CA molar ratio 1:2.09), polyoxyethylene (20) cetyl ether (CE20)/CA conjugate (CE20CA, CE20/CA molar ratio 1:0.93), and polyoxyethylene (20) oleyl ether (OE20)/CA conjugate (OE20CA, OE20/CA molar ratio 1:0.89) were obtained from a previous work [15].

2-2. Experimental animals

Hairless mice (HRM2 (HR-1/Hos × C3H/He Hos), 4 weeks old, 18-25 g) were provided by central Lab Animal Inc. (Seoul, South Korea). They were housed in wire mesh cages, accommodated in a room where the temperature was 18~26 ºC and the relative humidity was 30-70%, illuminated from 08:50 h to 18:50 h, and fed with a rodent diet and water ad libitum. Before being subjected to the *in vivo* experiment, they were acclimated for one week. The animal protocol used in the *in vivo* experiment was reviewed and approved based on ethical procedures and scientific care by the Kangwon National University Institutional Animal Care and Use Committee (KW-150616-1).

2-3. Preparation of emulsions using cinnamoyl surfactants

Cinnamoyl surfactants, namely CE20CA, OE20CA, and TW20CA, were used as emulsifiers. 1 ml of mineral oil was put in 4 ml of cinnamoyl surfactant solution (1% (w/v) in distilled water) contained in a 10 ml vial, vortexed on a vortex mixer (G-560, Scientific Industries, USA), and homogenized by sonicating the mixture for 10 min at room temperature using a bath type sonicator (VC 505, Sonic & Materials, Newton, CT, USA). The sonication was performed in a manner that the pulse was on for 20 sec then off for 20 sec. The stability of emulsion was investigated in terms of change in the oil droplet size. The optical micrographs were taken on an optical microscope (CX31, OLYMPUS, Tokyo, Japan) soon, 1 week, 2 weeks, 3 weeks, and 4 weeks after the emulsion preparation and the diameter of oil droplets was determined using an image analyzer (Image-Pro® Plus 5.1, Media Cybernetics, Santa Barbara, CA, USA).

2-4. *In vivo* UV-protecting efficacy of emulsifiers and emulsions

A UV-impermeable black adhesive film was cut into a rectangular one (3.5cm × 2.5 cm), then six square pieces (0.5 cm × 0.5 cm) were cut out from the rectangular film so that six windows were formed in the film with each window being spaced 0.5 cm apart from each other (Fig. 5). The numbers 1 to 6 indicate a window number in the film on the back of mouse who was not subjected to a sample application, and the numbers 1' to 6' indicate a window number in the film on the back of the mouse that was subjected to a sample application. Adhesive film having six windows was attached to the back of hairless mice, and UV light (6 W, 312 nm) (VL-6 MC, Vilber Lourmat) was irradiated on the back with the light source spaced 7.0 cm apart from the back. The amount of light irradiated to each window was adjusted to a certain value (mJ/cm^2) by blocking the windows sequentially with irradiation time using the same adhesive film. Table 1 shows the amount of light irradiated to each window, and the irradiation time. OE20CA was chosen as an emulsifier for the investigation of UV-protecting efficacy because it exhibited a high molar extinction coefficient (11,443 M^{-1}cm^{-1}) [15] and it was highly water-soluble. O/W emulsion prepared using TW20CA was chosen as an emulsion for the investigation of UV-protecting efficacy because TW20CA exhibited a high molar extinction coefficient (25,213 M^{-1}cm^{-1}) [15] and it was stable. PARSOL was used as a control UV-protective agent. OE20CA solution and PARSOL one were prepared by dissolving each of them in distilled water so that the concentration was 5% (w/v). O/W emulsion was prepared by emulsifying 2 ml of mineral oil in 8 ml of TW20CA solution (2% (w/v), in distilled water). Adhesive film having six windows was attached to the back of the hairless mice (HRM2), and 0.5 ºC each of the preparations (OE20CA solution, PARSOL solution, emulsion stabilized with TW20CA) was applied to each of the windows. Windows were exposed to UV light (6 W, 312 nm) for the specified time period shown in Table 1 by blocking the windows using the film at the given time shown in Table 1. UV irradiation was stopped when the last window (window 6 and window 6') was blocked. 6 h after UV irradiation was stopped, the windows were carefully examined to find a window where a black spot appeared for the first time, thus to determine the minimum amount of UV light to induce a black spot (MAUL). The data obtained from four animals were averaged.

3. Results and discussion

3-1. Preparation of emulsions using cinnamoyl surfactants

Fig. 2A shows the optical micrographs of the oil droplets of emul-

Table 1. The amount of UV irradiated to each window in the adhesive film on the back of mouse and irradiation time

Window number	Without sample application						With sample application					
	1	2	3	4	5	6	'1	'2	'3	'4	'5	'6
Amount of light (mJ/cm^2)	244	305	381	476	595	744	476	595	744	930	1163	1454
Irradiation time (sec)	147	183	228	276	357	446	276	357	446	558	698	872

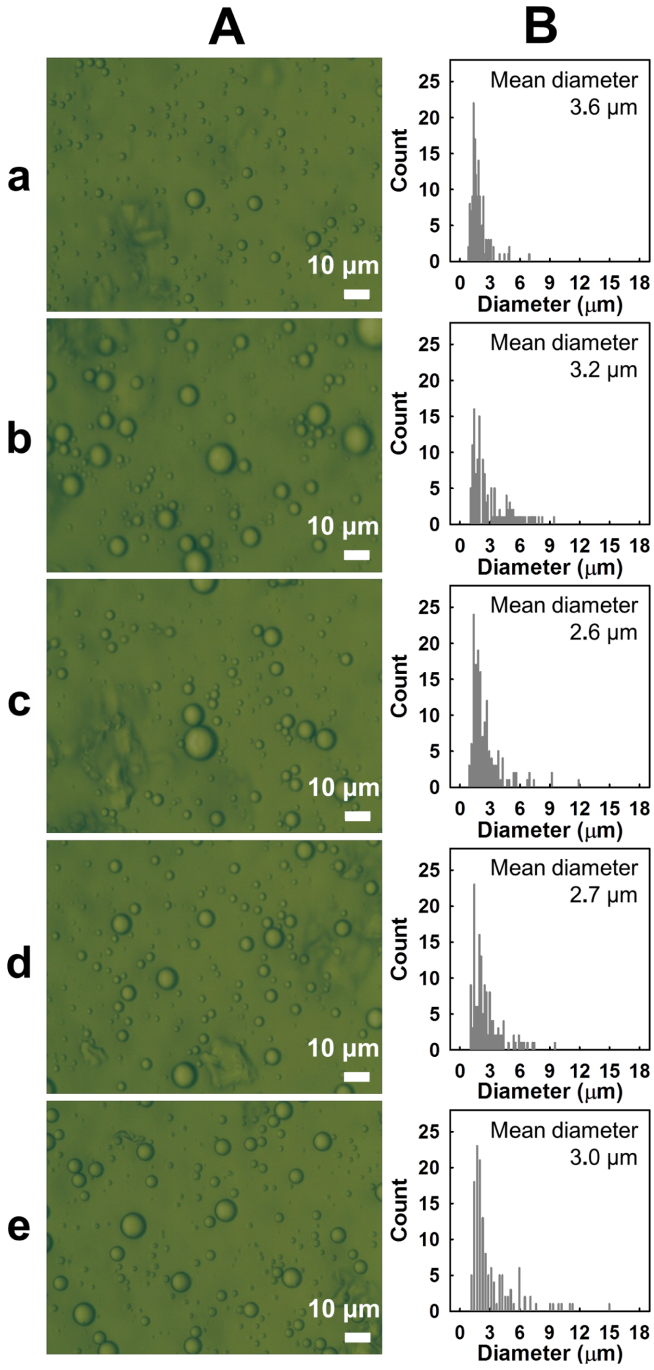

Fig. 2. Optical micrographs (A) and size distributions (B) of the oil droplets of emulsion prepared using TW20CA as an emulsifier, 0 week (a), 1 week (b), 2 weeks (c), 3 weeks (d), and 4 weeks (e) after the emulsion preparation.

sion prepared using TW20CA as an emulsifier 0 week, 1 week, 2 weeks, 3 weeks, and 4 weeks after the emulsion preparation. The micrographs show no marked difference in the oil droplet size, indicating that the emulsion was stable for four weeks in terms of the droplet size. TW20CA was reported to keep the oil droplet size almost constant during the whole experimental period (3 days) [17]. The emulsion stability is affected mainly by the amount of emulsifier and the hydrophilic/lipophilic balance (HLB) number. The amount of emulsifier should be high enough to cover the surface area of oil droplets. When the concentration of TW20CA was 1% (w/v) in water, the amount of TW20CA was reported to be high enough to emulsify mineral oil in the water phase in the oil/water volumetric ratio of 1:4 [17]. The HLB number of emulsifier used for the preparation of O/W emulsion falls within 8-18 [18]. The HLB of TW20 is known to be 16.7. Since the cinnamoyl group is lipophilic, the HLB number of the surfactant would decrease upon the conjugation of cinnamoyl group. The number of cinnamoyl groups per one molecule of TW20CA was about only 2; thus conjugation was thought not to make the HLB number out of the range. Fig. 2B shows the size distributions of the oil droplets of emulsion prepared using TW20CA as an emulsifier, soon, 1 week, 2 weeks, 3 weeks, and 4 weeks after the emulsion preparation. Most of oil droplets were less than 5 μm in diameter soon after the emulsion preparation. The droplets whose diameter was greater than 5 μm were frequently found one week after the emulsion preparation. The count of the large droplets slightly increased with time lapse possibly due to the fusion of droplets. However, the mean diameter did not change markedly with time lapse. For example, the mean diameter of oil droplets was 3.6 μm, 3.2 μm, 2.6 μm, 2.7 μm, and 3.0 μm, respectively, 0 week, 1 week, 2 weeks, 3 weeks, and 4 weeks after the emulsion preparation. This means the emulsion prepared using TW20CA was stable for four weeks in terms of oil droplet size. Fig. 3A shows the optical micrographs of the oil droplets of emulsions prepared using CE20CA as an emulsifier, 0 week, 1 week, 2 weeks, 3 weeks, and 4 weeks after the emulsion preparation. Soon after the emulsion preparation (0 week), the oil droplets were larger than the oil droplets of the emulsion prepared using TW20CA. The size seemed to increase markedly for the first week. The HLB number of OE20 is known to be 15.7 and it can be used as an emulsifier for the preparation of O/W emulsion [19]. However, upon the conjugation of CA, the HLB number would decrease and the ability of surfactant to stabilize oil droplets could also decrease, leading to the fusion of oil droplets and an increase in the diameter. Fig. 3B shows the size distributions of the oil droplets of emulsion prepared using CE20CA as an emulsifier, 0 week, 1 week, 2 weeks, 3 weeks, and 4 weeks after the emulsion preparation. Soon after the emulsion preparation, the oil droplets ranged from 1 μm to 40 μm, most of them falling within oil 1 μm to 10 μm, and the mean diameter was calculated to be about 5 μm. One week after the emulsion preparation, the distribution of oil droplets became broader, and emulsion droplets whose diameter was greater than 40 μm were frequently found possibly due to the fusion of oil droplets. As described previously, upon the conjugation of CA, CE20 would become hydrophobic, its HLB would decrease, and the ability of the surfactant to stabilize oil droplets could also decrease, leading to the fusion of oil droplets. For the last three weeks, the size distributions did not change markedly, and the mean diameter did not change outstandingly either. For example, 1 week, 2 weeks, 3 weeks, and 4 weeks after the emulsion preparation, the mean diameter of oil droplets was 18.1 μm, 22.4 μm, 20.0 μm, and 16.4 μm, respectively. This is possi-

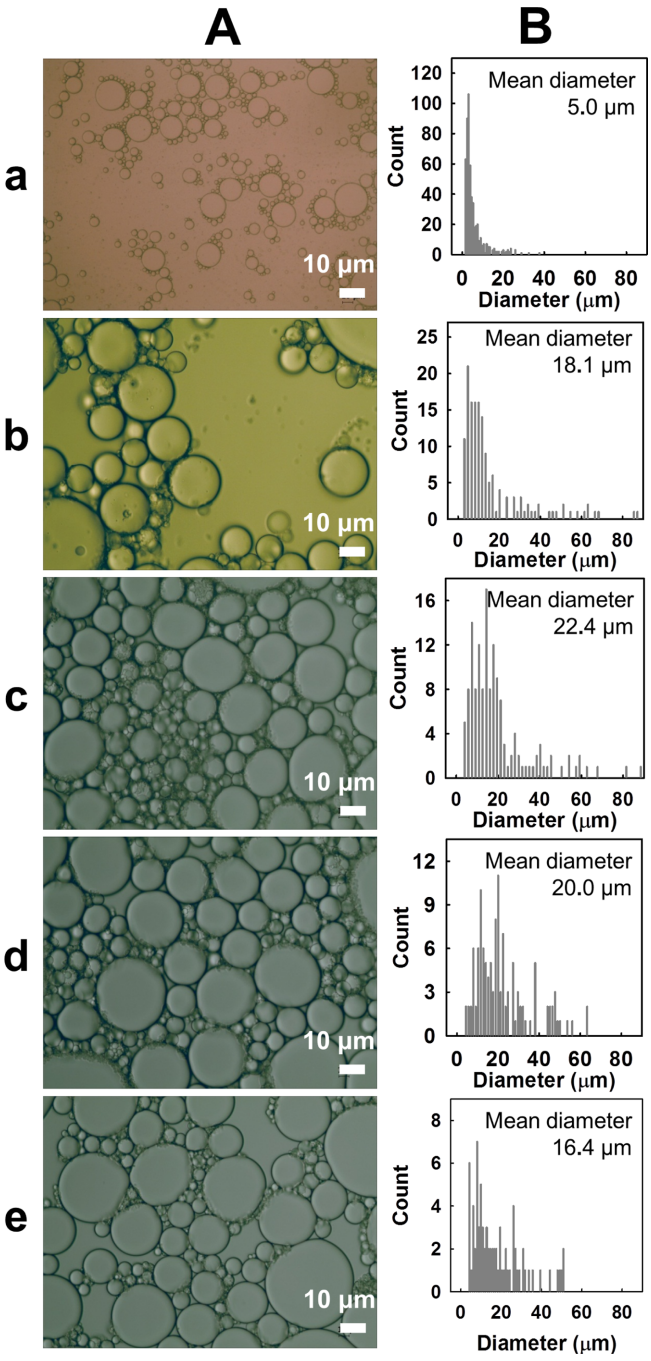

Fig. 3. Optical micrographs (A) and size distributions (B) of the oil droplets of emulsion prepared using CE20CA as an emulsifier, 0 week (a), 1 week (b), 2 weeks (c), 3 weeks (d), and 4 weeks (e) after the emulsion preparation.

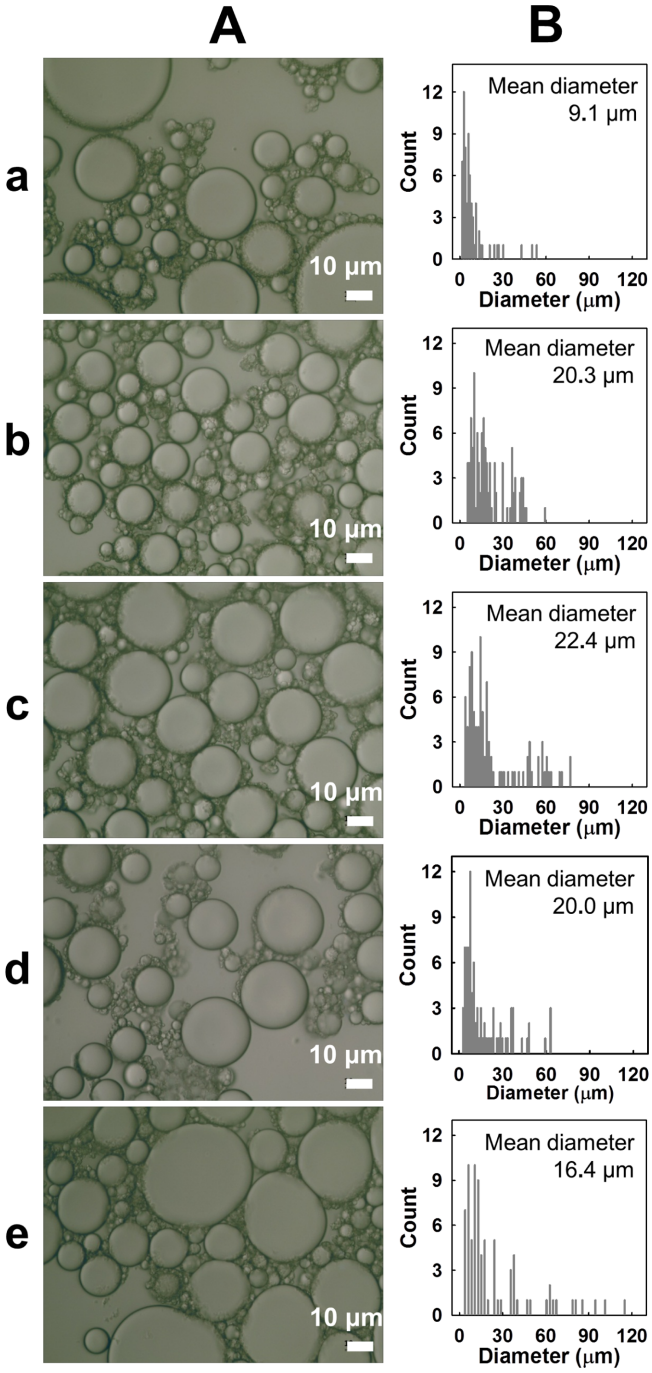

Fig. 4. Optical micrographs (A) and size distributions (B) of the oil droplets of emulsion prepared using OE20CA as an emulsifier, 0 week (a), 1 week (b), 2 weeks (c), 3 weeks (d), and 4 weeks (e) after the emulsion preparation.

bly because that the surface of the oil droplets became saturated with CE20CA as the droplets increased in size. To prepare stable emulsion, the HLB number of an emulsifier should fall within the adequate range (8-18) and the amount of the emulsifier should be high enough to cover the surface of oil droplets. If the fusion of droplets occurs, the size of oil droplets increases, leading to a decrease in the total surface area of droplets. Accordingly, the amount of the emulsifier per the unit surface area increases and the surface might be saturated with the emulsifier, leading to the stabilization of oil droplets. This could explain why the droplets were stable in terms of size for the last three weeks. Fig. 4A shows the optical micrographs of the oil droplets of emulsions prepared using OE20CA as an emulsifier, 0 week, 1 week, 2 weeks, 3 weeks, and 4 weeks after the emulsion preparation. Soon after the emulsion preparation, the oil droplets ranged from 3 μm to 53 μm in diameter, most of droplets fell within the range of 3 μm to 15 μm, and the mean diameter of oil droplet was

about 9.1 μm. The size distribution of oil droplets observed one week after the emulsion preparation was markedly different from that observed soon after the preparation. That is, the count of larger oil droplets (whose droplet diameter was greater than 15 μm) increased for the first week. In addition, the mean diameter of oil droplet observed one week after the preparation was 20.3 μm, and it was much larger than the mean diameter observed soon after the preparation (9.1 μm). The broader distribution and the larger size are possibly due to the fusion of oil droplets. The HLB number of OE20 is known to be 15, and it can be used as an emulsifier for the preparation of O/W emulsion. As described previously, the HLB number of the surfactant would decrease by the conjugation of CA because CA has a hydrophobic phenyl group. Due to the decrease in the HLB number, the ability of the emulsifier to stabilize oil droplets would decrease, which could account for why the oil droplets markedly increased in size for the first week. Besides HLB number, the orientation of the emulsifier at the oil/water interface has a great effect on the stability of oil droplets because the O/W interfacial area that one molecule of emulsifier can cover depends on the orientation. OE20 has a polyoxyethylene (PEO) as a hydrophilic head group and it has oleyl group (C18) as a hydrophobic chain. The hydrocarbon chain of the surfactant would be dissolved in the oil phase and the hydrophilic PEO chain would be dissolved in the water phase. In this circumstance, the emulsifier can orient vertically with respect to the tangential line at the oil/water interface where the emulsifier is adsorbed; thus the O/W interfacial area one molecule of emulsifier can cover would corresponds to the cross-section area of the emulsifier. On the other hand, OE20CA has two hydrophobic moieties (cinnamoyl group and oleyl group) at its terminals with hydrophilic PEO in between them. In this circumstance, the emulsifier would be aligned parallel to the tangential line at the oil/water interface because the hydrophobic moieties located at the terminals are dissolved in oil droplet and the hydrophilic PEO is dissolved in continuous water phase; thus the O/W interfacial area one molecule of emulsifier can cover would correspond to the longitudinal area of the emulsifier. Accordingly, the O/W interfacial area one molecule of emulsifier can occupy would be larger when OE20CA is adopted as an emulsifier. Nevertheless, the oil droplet stabilized with OE20CA was unstable for the first week in terms of size. PEO can stabilize colloidal particles via steric stabilization mechanism because it takes an extended form in water due to its high hydrophilicity and it is flexible [16,20]. The degree of freedom of PEO of OE20CA would be much less than that of PEO of OE20 because both two terminals of PEO of CE20CA are solubilized in oil droplets and immobilized there. Thus, the steric stabilization effect of PEO of OE20CA would be less than that of OE20. This would account for why the emulsion stabilized with OE20CA was unstable in terms of size for the first one week. On the other hand, the size distribution of oil droplets observed during the rest period of experiment (two weeks to four weeks after the emulsion preparation) was not markedly different from that observed one week after the emulsion preparation. The mean diameter of oil droplet observed for the last three weeks did not markedly change either. The oil droplet increased in diameter for the first one weak and it would lead to a decrease in the total area of oil/water interface. As a result, the interfacial density of OE20CA would increase and the oil droplets could be more sterically stabilized. This would explain why there was no marked change in the size distribution and the mean diameter for the last three weeks. Among the three kinds of emulsions, the emulsion stabilized with TW20CA was the most stable. Since the TW20/CA molar ratio of TW20CA was about 1/2, TW20CA was believed to have, on average, one PEO segment which was not conjugated with cinnamoyl group; thus the degree of freedom of the PEO segment would be relatively high, leading to a higher steric stabilization effect. Since the CE20/CA molar ratio of CE20CA was 1/0.93 and the OE20/CA molar ratio of OE20CA was 1/0.89, most of the PEO chains of CE20CA and OE20CA would be conjugated with cinnamoyl group, so the degree of freedom of the PEO segment might be relatively low, resulting in a lower steric stabilization effect. This could account for why the emulsion stabilized with TW20CA was the most stable.

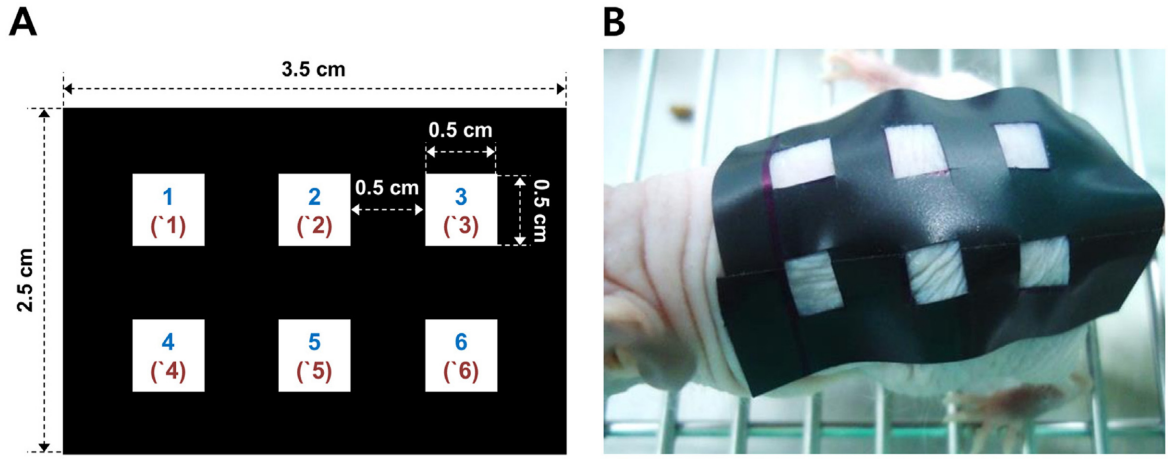

Fig. 5. Adhesive film (3.5 cm × 2.5 cm) having six windows (0.5 cm × 0.5 cm) spaced 0.5 cm apart from each other (A). A mouse (HRM2) having adhesive film on its back (B).

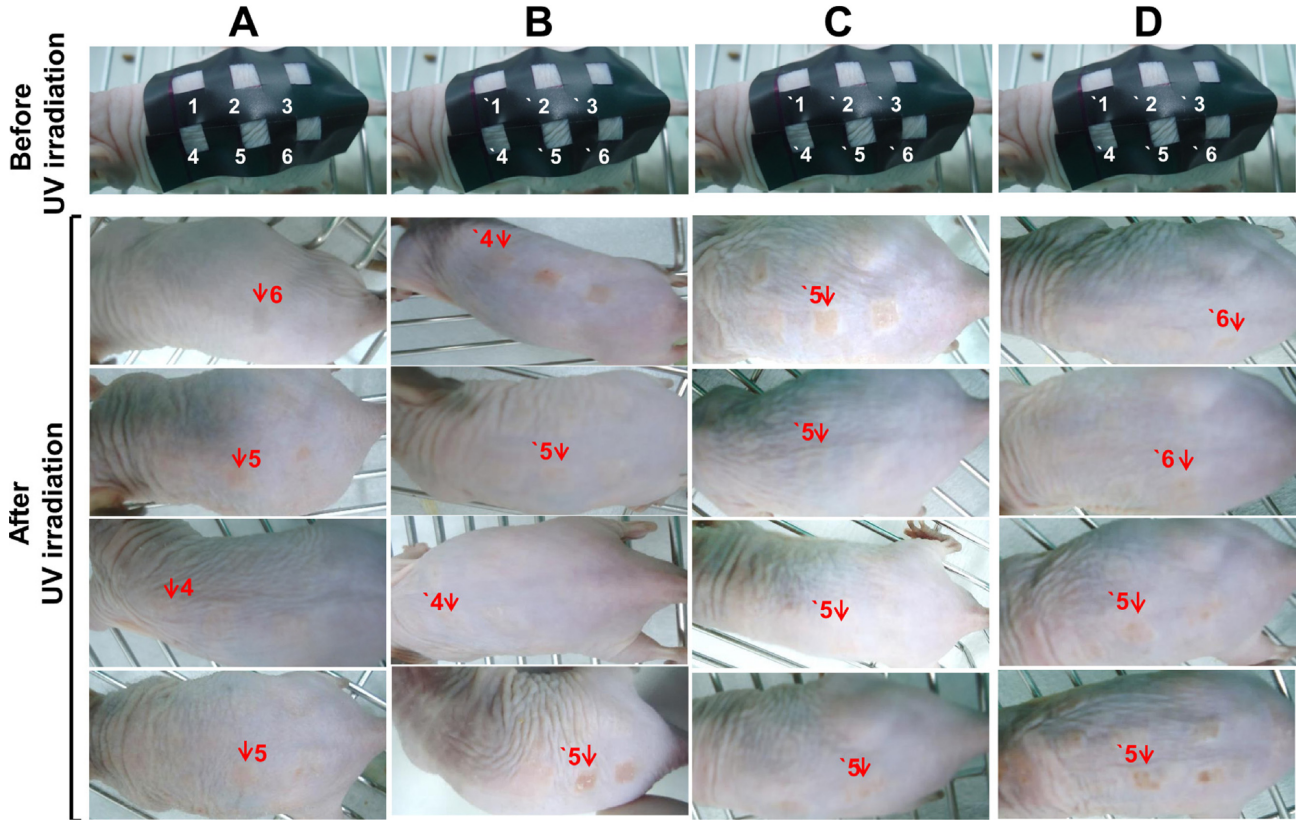

Fig. 6. Photos of backs of the mice treated with nothing (A), PARSOL solution (B), OE20CA solution (C), and emulsion stabilized with TW20CA (D) before and after UV was irradiated.

3-2. *In vivo* UV-protecting efficacy of emulsifiers and emulsions

Fig. 6 shows the photos of the backs of the mice treated with nothing, PARSOL solution, OE20CA solution, and emulsion stabilized with TW20CA before and after UV was irradiated. When the mice were treated with nothing, MAUL was 744 mJ/cm^2, 595 mJ/cm^2, 476 mJ/cm^2, and 595 mJ/cm^2, and the mean value was 602.5 mJ/ cm^2. When the mice were treated with PARSOL solution, MAUL was 930 mJ/cm^2, 930 mJ/cm^2, 1163 mJ/cm^2, and 1163 mJ/cm^2, and the mean value was 1046.5 mJ/ cm^2. The mean MAUL obtained with mice treated with PARSOL solution was about 73% higher than the mean value obtained with mice treated with nothing, indicating that PARSOL was efficacious in protecting the skin again UV light. PARSOL (butylmethoxydibenzoyl methane) is a well-known UV-protective agent. It can protect the skin from being tanned by absorbing UV light [21]. When the mice were treated with OE20CA solution, MAUL was 1163 mJ/cm^2, 1163 mJ/cm^2, 1163 mJ/cm^2, and 1163 mJ/cm^2, and the mean value was 1163 mJ/cm^2. The mean MAUL obtained with mice treated with OE20CA solution was about 11% higher than the mean value obtained with mice treated with PARSOL solution, indicating that OE20CA was more efficacious than PARSOL. The cinnamoyl group of OE20CA can absorb UV light; thus it can protect the skin from being tanned. Cinnamoyl group exhibits two absorbance peaks, one in the range of 200 nm to 230 nm and the other in the range of 230 nm to 320 nm, and it shows the maximum absorbance around 280 nm. The molar extinction coefficient of OE20CA was reported to be about 12000 M^{-1}cm^{-1} [15]. When the mice were treated with emulsion stabilized with TW20CA, MAUL was 1454 mJ/cm^2, 1454 mJ/cm^2, 1163 mJ/cm^2, and 1163 mJ/cm^2, and the mean value was 1308 mJ/cm^2. The mean MAUL was about 25 % higher than the mean value obtained with mice treated with PARSOL solution and about 13% higher than the mean value obtained with mice treated with OE20CA solution, indicating that the emulsion stabilized with TW20CA was more efficacious than OE20CA solution in protecting the skin from being tanned. The molar concentration of TW20CA in the emulsion (1.6% (w/v) corresponds to 10.4 mM) was about four-times lower than that of OE20CA in solution (5% (w/v) corresponds to 39.0 mM). Neither TW20 nor OE20 absorbs the UV light. The amount of UV light absorbed by the emulsifier depends mostly on the concentration of cinnamoyl group. The TW20/cinnamoyl group molar ratio of TW20CA was about 1/2.1, and the OE20/cinnamoyl group molar ratio of OE20CA was about 0.89/1 [15]. Thus, the molar concentration of cinnamoyl group in the emulsion stabilized with TW20CA was calculated to be about 21.4 mM, and that of cinnamoyl group in OE20CA solution was calculated to be about 34.7 mM. Since the molar concentration of cinnamoyl group in the emulsion was lower than that of cinnnamoyl group in OE20CA solution, the emulsion would absorb UV light less than OE20CA solution; thus the UV-protective efficacy of the emulsion would have been lower than that of OE20CA solution. However, the MAUL of the emulsion was higher and the emulsion exhibited a higher efficacy in

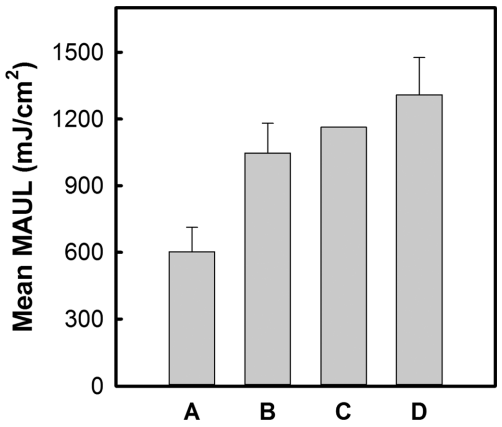

Fig. 7. Mean MAUL obtained from mice treated with nothing (A), PARSOL solution (B), OE20CA solution (C), and emulsion stabilized with TW20CA (D).

protecting the skin against UV light. UV-protective agents protect the skin against UV light because they can absorb or scatter UV light [21]. The oil droplets could scatter UV light, so they were thought to contribute to the UV-protecting efficacy of emulsion. In addition, the cinnamoyl groups of OE20CA would homogeneously distribute throughout its solution because OE20CA is readily solubilized in water. Whereas, the cinnamoyl groups of TW20CA would be aligned at the oil/water interface because TW20CA is amphiphilic and it is likely to be located at the interface. In this circumstance, the cinnamoyl groups aligned at the interface could absorb UV light more effectively than the cinnamoyl groups dissolved in bulk aqueous phase. The light scattering which could possibly take place due to the oil droplets of emulsion and the alignment of cinnamoyl groups at the interface would explain why the emulsion stabilized with TW20CA was more efficacious in protecting the skin from being tanned than OE20CA solution, even though the emulsion contained less cinnamoyl group than OE20CA solution. The mean MAUL obtained from mice treated with nothing, PARSOL solution, OE20CA solution, and emulsion stabilized with TW20CA is represented in Fig. 7.

4. Conclusion

Cinnamoyl surfactants, TW20CA, CE20CA, and OE20CA, successfully emulsified mineral oil in water when the surfactant concentration was 1% (w/v) in water and the oil/water ratio was 1/4 (v/v). The mean diameter of oil droplets stabilized with TW20CA, CE20CA, and OE20CA was 3.6 °C, 5.0 °C, and 9.1 °C, respectively. Among the three kinds of emulsions, the one stabilized with TW20CA was the most stable in terms of size, possibly because PEO segments not being conjugated with cinnamoyl group were contained in TW20CA, and they could sterically stabilize the oil droplets effectively. *In vivo* experiment for the examination of UV protecting efficacy revealed that the mean MAUL of PARSOL, OE20CA, and emulsion stabilized with TW20CA was 1046.5 mJ/cm^2, 1163 mJ/cm^2, and 1308.5 mJ/cm^2, respectively. That is, UV-protecting efficacy was in the order of emulsion stabilized with TW20CA > OE20CA > PARSOL. Not only the UV-absorbing property of cinnamoyl group but also the UV-scattering property of the oil droplets was thought to be responsible for the high UV protecting efficacy of the emulsion.

Acknowledgements

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