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# Stabilization of L-ascorbic acid in cosmetic emulsions

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ABSTRACT

The prevention of the oxidation of L-ascorbic acid in cosmetic emulsions was investigated. First, its stability was tested to determine the optimum ratio, and the effects of changes in the pH, color, and concentration of L-ascorbic acid in the emulsions were investigated. The kinetics of L-ascorbic acid in emulsions were studied through HPLC. The inclusion of glycerine in the dispersion was more effective in maintaining the initial L-ascorbic acid content than the inclusion of propylene glycol, butylene glycol or DI water. A zero-order reaction model best fitted the butylene glycol-in-oil emulsion, whereas a first-order model best fitted the water-in-oil emulsion.



## Introduction

Ascorbic acid is an enantiomer whose optical properties are classified as the L and D forms [1]. L-ascorbic acid (LAA), also called vitamin C, is a useful material in the human body [2]. The application of LAA to human skin provides many properties that improve the characteristics of the skin including whitening, wrinkle improvement and antioxidation. LAA can suppress the production of melanin, which makes skin darker, by aiding the reduction of melanin in the melanocytes; this is called the whitening effect [3,4]. In addition, LAA improves wrinkles by acting as a collagen synthesis coenzyme in the dermis [5]. Furthermore, LAA can prevent UV-induced damage to the DNA and proteins. Instead of reacting with DNA or proteins, the hydroxyl radicals derived from the reactive oxygen species that are generated by UV light react with LAA: this is called the antioxidant effect [6–8]. The efficacy of LAA is related to its oxidation. LAA is a type of reductone structure, as shown Fig. 1. Its oxidation occurs by first ionizing both hydroxyl groups at the second and third carbons of an enediol group and subsequently producing dehydroascorbic acid by the loss of 2 protons and 2 electrons [9–11].

Although LAA has many advantages, it is not generated in the human body. Hence, it must be acquired from an outside source via the skin or via oral administration: these sources include cosmetics, food, medicine and medical supplies [6]. In addition, LAA can easily be oxidized by external factors such as moisture, light, heat and metal ions. The oxidized form of LAA, dehydroascorbic acid, has no antioxidant effect because it cannot make ascorbate ions in the neutral pH of the human body [12].

Various studies of cosmetics, food, medical and medical supplies have attempted to prevent the oxidation of LAA by external factors [13–20]. The study of LAA derivatives is an especially active field. Percutaneous absorption of one LAA derivative, ascorbyl palmitate ascorbyl-2-glucoside, is less than that of ascorbic acid [15]. Additionally, magnesium-ascorbyl phosphate has a smaller antioxidant effect than LAA [16,17]. Therefore, the ability to stabilize LAA in an emulsion is critical for its effective delivery into the human body.

Two approaches have been generally applied to cosmetic materials. First, the structures of the materials can be changed to improve the effects and overcome drawbacks such as limitations in the skin permeation and solubility. Second, procedures to stabilize the effective materials in various emulsions have been developed. These two approaches are both important. However, the latter approach is preferred with respect to the time and the cost of developing cosmetic products. This approach should therefore be studied more thoroughly to create cosmetics that contain effective components.

Emulsion formulations can be classified as simple emulsions and double emulsions [21]. Simple emulsions are divided into the water-in-oil (W/O) and oil-in-water (O/W) types, which are characterized by a dispersed phase and a continuous phase. In contrast, double emulsions include the water-in-oil-in-water

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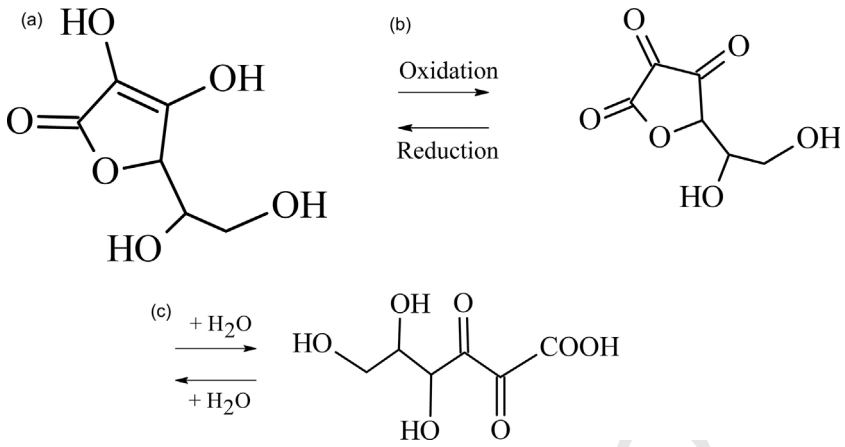


**Fig. 1.** Oxidation of LAA in aqueous solution: (a) LAA, (b) dehydro-LAA, and (c) 2,3-diketo-L-gulonic acid.

(W/O/W) or oil-in-water-in-oil (O/W/O) types. The type of emulsion used should be compatible with the target materials.

The present study used a simple emulsion process that involved monodisperse emulsion droplets rather than a double emulsion [22,23]. The process to formulate a simple emulsion is shorter than that required for a double emulsion, which minimizes the LAA oxidation during the emulsion formulation process. Additionally, this study was designed to assess the ideal raw materials to prevent the oxidation of LAA in the emulsions due to moisture. Four types of emulsions were used in this study: W/O, propylene glycol-in-oil (PG/O), butylene glycol-in-oil (B/O), and glycerine-in-oil (G/O) emulsions.

Another research group used LAA synthesized with a functional group or additives to stabilize the LAA. The safety and skin permeability of these materials in cosmetic emulsions were not efficiently confirmed [11,24]. Unlike the above-mentioned research group, we used polyol, which has been used as a moisturizer in cosmetic emulsions for many years and is a stable material in cosmetic emulsions. Therefore, the best material to stabilize LAA in cosmetic emulsions can be directly used in real cosmetic emulsions. Additionally, the expiration date of cosmetics containing LAA will be extended without the addition of preservatives for stabilizing the LAA.

## Materials and methods

### *Materials*

LAA was purchased from DSM (Havelock Road, Singapore). Glycerine was obtained from IOI Oleochemicals (Penang, Malaysia). Propylene glycol was purchased from SKC (Ulsan, Korea). 1,3-Butylene glycol was purchased from Daicel Corporation (Tokyo, Japan). Cyclohexasiloxane (SF1258) was purchased from Momentive (Seoul, Korea). Octamethylcyclotetrasiloxane (EA3105) was purchased from Elementis Specialties (Shanghai, China). Lauryl PEG-9 polydimethyl siloxyethyl dimethicone (KF6038) was purchased from Shin-Etsu Chemical (Tokyo, Japan). Sorbitan isostearate (Span™ 120) was purchased from Croda Korea Chemical (Seongnam, Korea). Cetyl dimethicone copolyol (Abil EM 90) was purchased from Evonik (Ulsan, Korea). Potassium phosphate ($KH_2PO_4$, monobasic, 99.0%) and phosphoric acid ($H_3PO_4$, 85%) were purchased from Samchun Chemical (Pyeongtaek, Korea). Deionized (DI) water was used throughout the study. All of the chemicals were reagent grade and were used without any further purification.

### *Preparation for emulsion formulations and change of color*

To investigate the emulsion ratios for which no phase separation occurred, polyol-in-oil (P/O) emulsions were produced. Three kinds of polyols were used as the dispersed phase: glycerine, butylene glycol, and propylene glycol. The control formulation, a W/O emulsion, was prepared at the same ratio as the P/O emulsion. Fig. 2 shows the emulsion formulation process. In the first step, the polyol used as the dispersed phase was weighed. Subsequently, LAA was added and was fully mixed using an agitator at 300 rpm for 5 min. For the next step, the continuous phase was produced from the oil, surfactant, and rheological additive. These solutions were mixed together with an agitator at 300 rpm for 5 min. Finally, the emulsion was created by adding the dispersed phase slowly to the continuous phase and mixing uniformly with an agitator at 500 rpm for 10 min. Instead of the polyol, DI water was used to make the control formulation using the same process as the P/O emulsions. All emulsions were incubated at 25 °C or 45 °C [25,26]. The time-dependent color changes of the emulsions were evaluated using a modified organoleptic method [27]. All emulsions stored under different conditions were investigated visually in terms of color and phase separation.

### *Determination of stability from phase separation*

To select the best ratio for an emulsion, the W/O and P/O emulsions were stored at 25 °C or 45 °C. The phase separation of all emulsions over a period of 30 days was assessed using centrifugation (VS-5000i, Vision, Daejeon, Korea). Two grams of the sample was placed in a centrifuge tube, and a stability test was performed using the VS-5000i at 3000 rpm for 30 min. The sample was observed with respect to phase separation by visual examination [25].

### *Measurement of LAA content*

The emulsions were incubated under storage conditions at 25 °C or 45 °C. The LAA content of each emulsion was confirmed using an HPLC system (Agilent 1260 Infinity, Agilent Technologies, Waldbronn, Germany). A 0.15 g aliquot of each sample was weighed and diluted to a final volume of 50 mL with 80% isopropanol (IPA). The diluted sample was subjected to ultrasonication for 20 min to completely dissolve the sample. After the sample was filtered, it was injected into a 2-mL vial to measure the LAA content using HPLC.



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