Development of Oil-in-Water Emulsion Containing Tamarind Fruit Pulp Extract I. Physical Characteristics and Stability of Emulsion

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Abstract

The oil-in-water (o/w) emulsion containing natural AHAs was formulated and developed for application in cosmetic product including facial cleansing. Fruit pulp of tamarind was used as the source of the natural AHAs since its efficiency to skin has been proved in the past. In addition, the tamarind is generally found in Thailand and its fruit is not expensive source. For extraction process, the fresh fruit pulp of tamarind was extracted with water. The aqueous solution of the crude extract was subsequently dried by lyophilization, and the obtained extract powder was determined for its tartaric acid content by using HPLC. Various formulas of the free-extract emulsions consisting of various pairs of the nonionic emulsifier and types of the thickening agent were firstly formulated. The physical characteristics and stability of the prepared emulsions were evaluated and the best formula was then selected for preparing the emulsion containing the extract. The considerably physical characteristics included color, texture, pH and viscosity of the emulsions, and the stability of the emulsions was tested by using heat-cool cycling method. Resulting from this study, we found that the using 5.49% of Tween® 60 and 1.51% of Span® 80 as the emulsifier blend, coupled with the using 0.2% of Carbopol® 940 as the thickening agent provided the emulsion with the most favorable characteristics and the best stability for our extract-free emulsion system. Next, this free-extract emulsion was incorporated with the various amounts of the extract, and the physical characteristics and stability of these prepared emulsions were also investigated. We found that the final product containing the extract in amount corresponding to 0.5% of tartaric acid (formula of $S_{80}T_{60}C_{0.2}E_{0.5}$) showed good physical characteristics and both physical and chemical stability. The viscosity of this product was also comparable to that of the commercial product.
Keywords: Tamarind, Emulsion

Introduction

Botanical secrets have been passed down through generations of herbal folklore, and nowadays, the botanical extract is playing an increasingly important role in cosmetics. For cosmetic industry, isolation and purification of the active ingredient within the crude extract are sometimes not needed because such isolation and purification may lead to a loss in the biological activity (Khaiat, 2000; Lee *et al.*, 1997). Since the botanical extract usually contains hundreds of chemical structures, an incorporation of the extract into the cosmetic formula, however, may cause several problems. For examples, an incompatibility between ingredient used in the formula and component consisted of the extract lead to decrease in product stability and safety. In addition, the unfavorable color and odor that are usual properties of the crude extract may attenuate the consumer compliance. Therefore, it is the duty of formulator to solve these problems and to produce the products related to the consumer needs by using various formulation techniques and knowledge.

Several cosmetic formulas are available in market such as emulsions, suspensions and gels. Emulsion system including lotions and creams is an area of big potential for cosmetic products, and the various techniques of emulsion preparation have been widely studied. The emulsion is versatile in application, depending on the bioactives incorporated. For example, the emulsions containing alpha-hydroxy acids (AHAs) may improve the appearance of skin, thus leading to a younger look. Typically, emulsion system consists of an immiscible liquid (internal) phase finely dispersed in another liquid (external) phase i.e. oil dispersed in water (o/w emulsion) or water dispersed in oil (w/o emulsion). For skin care products, the o/w emulsion is much popular according to its washable and non-greasy properties. Furthermore, after applying to the skin, water evaporates and concentration of the water-soluble bioactives are subsequently increased in the adhering film. This promotes the absorption of such bioactives to the skin (Guy and Hadgraft, 1988; Riefenrath *et al.*, 1991; Rothman, 1955; Scheuplein, 1965).

Topical emulsion formulas containing AHAs are now frequently used or prescribed by dermatologists and they are also presented in a wide range of heavily promoted cosmetic products including facial skin cleanser. The low concentration (less than 4%) of AHAs has been suggested to use for daily application (Pierard *et al.*, 2000)**.** The primary action of AHAs is to exfoliate dead skin cells by weakening bonds that hold dead skin cells together, thus resulting in skin which looks brightness (Berardesca and Maibach, 1995; Smith, 1996; Van Scott and Yu, 1984). AHAs range from simple aliphatic compounds to complex molecules. Many of these substances can be derived from natural sources and are often referred to “fruit acids”. However, a number of synthetic sources provides access to compounds with structural analogous. The AHAs now used in cosmetics product are usually produced by chemical synthesis because the synthetic products offer higher purity and quality in a dependable consistency.

The debate over natural versus synthetic AHAs has ranged for several years. According to acidifying property of AHAs, they have a potential to irritate the skin. However, their irritation potential is also coupled with the ability to stimulate cell renewal. It has been found that the therapeutic index (the ratio of stimulation to irritation) of the natural AHAs surpasses that of the synthetic AHAs. It is likely that the natural AHAs contain natural soothing agents which can reduce their irritation potential, and not interfere with the stimulatory activity (Smith, 1994)**.** Therefore, in the clinical viewpoint, using naturally derived AHAs in cosmetic products will provide much more benefit comparing to synthetically derived AHAs.

Tamarind *(Tamarinduc indica* L.*)* is a common tree grown elsewhere in humid tropical areas including South East Asia. Its fruit pulp with acidic taste has been used for centuries as skin-scrubbing material to propose smoother and lighter skin appearance. The improving in visible effect of skin raises the question about components resided in the tamarind's fruit pulp and actions to skin of those components. Promising report showed that the fruit pulp of tamarind contains AHAs including tartaric acid (8-23.8 %), lactic acid (2 %), citric acid and malic acid. Besides AHAs, pectin and invert sugar were also found in the fruit pulp (Grieve, 1992; Morton, 1999). Both are hygroscopicity and can improve the better looking of the skin by their moisturizing action. These findings led to the interest of using the extract derived from the fruit pulp of tamarind for application in cosmetic products.

Therefore, the purpose of this study was to formulate and develop o/w emulsion containing the extract of the tamarind's fruit pulp for facial skin cleansing. The tamarind's fruit pulp was selected as the source of AHAs since it is cheap, and its efficiency to skin has been proved in the past. The effects of types of the emulsifiers and thickening agents, as well as concentrations of the extract on physical characteristics and stability of the prepared emulsions were focused in this study. Furthermore, the viscosity of the prepared product at before and after stability test was measured and compared to the viscosity of the commercial product to indicate the stability and the possibility of our product to be marketed in the future.

Materials and methods

Materials

All materials were used as received and were cosmetic grade. Cetyl alcohol, glycerin, isopropyl myristate, stearyl alcohol, sorbitan esters (Spans®) and polyoxyethylene derivatives of sorbitan esters (Tweens®) were supplied by Srichand United Dispensary Co., Ltd., Thailand. Acrylic acid polymer (Carbopol® 940) was supplied by Hong Huat Co., Ltd., Thailand. Methyl cellulose (MC) 1500 was supplied by SNP Co., Ltd., Thailand. Liquid paraffin was supplied by PP Co., Ltd., Thailand. Triethanolamine (TEA) was purchased from Riedel deHaen, Germany Analytical grade of tartaric acid were purchased from Riedel deHaen, Germany.

Method for preparing the extract

Fresh fruit pulps of tamarind with a brownish red color and an acid-flavored were purchased from the market in Phitsanulok Province, Thailand. One kilogram fruit pulp without seed was extracted with 4.5 L water for overnight at room temperature. The resultant paste was then filtered through a cloth in order to remove rubbish. The aqueous solution of fruit pulp was dried by lyophilization (FTS system Dura dry type FD 95C12, USA) and the obtained powder with brownish color was kept in a tight container at 4 °C.

Method for analyzing the quantification of tartaric acid

As tartaric acid is a major AHAs compound usually found in the fruit pulp of tamarind, this acid acted as a marker to evaluate the content of AHAs in the extract. The content of tartaric acid in extract powder or diluted emulsion was determined by isocratic HPLC technique (Model CM3200, Sitronic Co., USA). The column (supeosil LC8, 4.6 x 250 mm) was eluted with 0.05 M potassium dihydrogen phosphate (pH 3). Quantification of tartaric acid was based on peak area at 215 nm. All the experiments were performed in triplicates.

Preparation of the extract-free emulsion

Formulations of the extract-free emulsions

The emulsion formula used in the present study was modified from the previous work that had studied the formulation and development of tomato's AHAs cream (Chinpatanawong *et al*., 1998). The emulsifier blend of the nonionic emulsifiers (Tweens® + Spans®) in total amount of 7% by weight of emulsion was favorably employed in this study according to the preliminary study indicating the good stability of this modified emulsion system with 7% of the nonionic emulsifier (data not shown).

In this study, we would like to formulate o/w emulsion for facial cleansing purpose. Therefore, the water content in formula comprised more than 80% by weight of the emulsion. Generally, the type of emulsions (o/w or w/o) is determined by the phase ratio of oil and water if these numbers are high (>3). For example, in this study with 11.5% of oil and 81.5% of water (an o : w phase ratio of 8), the emulsion was expected to be o/w (Friberg *et al*., 1988). The appearance of emulsion obtained from this modified formula was also expected to be a fluid liquid, namely lotion because the lowering in amounts of the stiffening agents used. The chemical compositions of the modified formula and the function of each composition are shown in Table 1.

Table 1. Components presented in the modified formula

Component	% w/w	Basic Function
Oil phase		
Isopropyl myristate	5.00	emollient
Stearyl alcohol	1.00	stiffening agent, emollient
Stearic acid	1.50	stiffening agent
Liquid paraffin	3.00	occlusive emollient
Spans®	a	nonionic surfactant
Water phase		
Tweens®	b	nonionic surfactant
Propylene glycol	5.00	humectant
Glycerin	5.00	humectant
Disodium EDTA	0.15	chelating agent
Methyl paraben	0.20	preservative
Propyl paraben	0.02	preservative
Deionized water added to	100.00	diluent

Note: The total emulsifiers used (a+b) equals 7% by weight of emulsion.

Preparation of the extract-free emulsion with o/w type

For o/w emulsion preparation, oil phase is usually added to water phase. However, phase inversion technique, that is addition of the water phase to the oil phase, was preferred in this study since it has been reported that the emulsions formed by the phase inversion technique contain a finely dispersed internal phase and consequently is stable (Schulman and Cockbain, 1940a). The oil phase was heated about 5 to 10°C above the melting point of the highest melting point ingredient while the water phase is heated to the same temperature of the oil phase. Thereafter, the water phase was continuously added to the oil phase, and constant agitation was provided throughout the time of addition. The agitation was continued until the product was cooled to room temperature.

Studies in effects of types and concentrations of emulsifiers and thickening agents on the physical characteristics and stability of the extract-free emulsion

Theses studies were established to minimize the amounts of the trial emulsions, including the total amounts of the extract used in the present study. The studied were based on the fact that the degree of creaming or coalescence (separation) is minimum at the optimal HLB value, including at the optimal type and concentration of the thickening agent. The final formula that showed the good physical characteristics and stability was then selected for preparing the emulsion containing the extract.

Effects of types and concentrations of emulsifiers

As the emulsifiers act a major role in the properties of emulsions, the effects of types and concentrations of emulsifiers on the physical characteristics and stability of the prepared o/w emulsions were investigated. The nonionic emulsifiers including Tweens® and Spans® were favorably employed in the present study because of their less irritability and compatibility with almost components, and their cheap cost. Hydrophile-lipophile balance (HLB) system was used to assist in making decisions about the relative amounts and the types of Tweens® and Spans® needed in stable products. The information related to HLB system, including calculation of HLB value is present in Appendix.

In o/w emulsion, It has been reported that the utilizing a blend of a lipophilic and hydrophilic emulsifier can produce more stable emulsions than the utilizing a single emulsifier with the same HLB number (Griffin, 1949; Griffin, 1954). Therefore, the blend of various pairs of lipophilic (Span® 80 and 40) and hydrophilic emulsifiers (Tween® 20 and 60) was incorporated in the emulsion system, and the obtained product with the most favorable appearances and good stability was then selected for further study. The relative amounts of the emulsifier blends used are shown in Table 2. The reason of using these pairs of the nonionic emulsifiers (Span® 80 + Tween® 20, Span® 80 + Tween® 60, Span® 40 + Tween® 20, Span® 40 + Tween® 60) in this study will be discussed in the results and discussion part.

Effects of types and concentrations of thickening agents

According to the previous study, the formula that provided the good physical characteristics and stability was selected for studying in the effects of the types of the thickening agents on the physical characteristics and stability of the emulsion. Either Carbopol 940 as a representative of synthetic polymer or methyl cellulose 1500 as a representative of semi-synthetic polymer was employed, and the characteristics of the emulsions obtained from such polymer were subsequently investigated. The percentage (by weight) of the thickening agents was ranged in 0.2 to 1.00 % by weight of emulsion. In this study, natural polymers were not taken into consideration because their two main disadvantages. First, they usually show batch to batch variation in composition which affects the consistency of the final products. Secondly, the susceptibility to bacterial or mold growth of the natural gums affects the stability of the products (Billany, 1990).

The formula that provided the emulsions with favor physical characteristics and good stability, namely *final extract-free formula*, was then selected for preparing the emulsions containing the tamarind fruit pulp extract and also studying the effects of the concentration of AHAs on the physical characteristics and stability of the emulsion.

Table 2. The extract-free emulsion formulas with various pairs of the emulsifier blend used

Component (% w/w)	**Formula**			
	$S_{80}T_{20}$	$S_{80}T_{60}$	$S_{40}T_{20}$	$S_{40}T_{60}$
Oil phase				
Span®80	**2.31**	**1.51**	-	-
Span®40	-	-	**2.86**	**1.95**
Isopropyl myristate	5.00	5.00	5.00	5.00
Stearyl alcohol	1.00	1.00	1.00	1.00
Stearic acid	1.50	1.50	1.50	1.50
Liquid paraffin	3.00	3.00	3.00	3.00
Water phase				
Tween®20	**4.69**	-	**4.14**	-
Tween®60	-	**5.49**	-	**5.05**
Propylene glycol	5.00	5.00	5.00	5.00
Glycerin	5.00	5.00	5.00	5.00
Disodium EDTA	0.15	0.15	0.15	0.15
Methyl paraben	0.20	0.20	0.20	0.20
Propyl paraben	0.02	0.02	0.02	0.02
Deionized water added to	100.00	100.00	100.00	100.00

Study in effects of the concentrations of AHAs on the physical characteristics and stability of the emulsion

The emulsions containing the tamarind fruit pulp extract were prepared by relying on the formula resulted from the previous study. The different amounts of the extract corresponding to 0.5, 1 or 1.4% of tartaric acid were incorporated into *the final extract-free formula*. The concentration of AHAs usually used in the commercial facial skin cleansing is 0.5-1 % by weight of formula. Thus, the concentration of AHA used in our study covered that ordinarily used in commercial practice and much higher. The higher concentration of AHAs was designed in order to show whether or not a higher in the amount of AHAs used in would affect the stability of the lotion. The preparation procedure of the emulsion containing the extract is as following. Carbopol®940 was dispersed in part of deionized water. Other water phase ingredients except for methyl and propyl paraben were added to the Carbopol®940-dispersing solution. The solution mixture of water phase was heated to 70°C while oil phase ingredients was heated to 75°C. The water phase was constantly added to the oil phase with rapid agitation. Agitation was continued until the emulsion was cooled down to 40-45°C. The extract powder was dissolved in part of deionized water and then added to the emulsion. After addition of methyl and propyl paraben, a certain amount of TEA was added to neutralize Carbopol®940 and the viscosity of the preparation was then increased. The final products were subsequently investigated for the physical characteristics including pH and viscosity, and the physical and chemical stability.

Methods for determining types, physical characteristics and stability of the prepared emulsion

Determination of types

This study was used to confirm whether the type of the prepared emulsions bases on the numbers of the o : w phase ratio obtained. The type of the emulsion was simply evaluated by dilution method. A certain amount of water was added to the prepared emulsion. If the emulsion had been miscible or could be diluted with the water, this emulsion was o/w type.

Determination of physical characteristics

The physical characteristics or appearances of the prepared emulsions were determined by visualization. These characteristics included color, texture, viscosity (easy or hard to pour off from the bottle) and pH. The pH of the prepared emulsions was measured by using Mettler Toledo Electrode (Mettler Toledo GmbH, Switzerland). The viscosity of the emulsion obtained from some formulas was measured by using Brookfield digital rheometer (Model DV-III, Brokkfield, USA).

Determination of stability

The physical stability of the prepared emulsions was determined by heat-cool cycling between refrigerator temperature and 45°C with storage at each temperature of 24 hr. Creaming (a reversible separation of the emulsion into dilute and concentrated region) or coalescence phenomenon (an irreversible destruction of emulsion) of the emulsions was observed after each cycle had finished. For the formulas that the tamarind fruit extract was incorporated, the amount of tartaric acid at before and after stability testing for 7 cycles was also measured by using HPLC to determine the chemical stability of the emulsions produced from such formulas.

Statistics

T-test was performed on data sets. Statistical significance was set at $P<0.05$.

Results and discussion

Quantification of tartaric acid in the extract

The aqueous extract of tamarind fruit pulp gave a light-brown powder after lyophilization. This powder was kept in tight container at 4°C for further studies. The content of tartaric acid in extract powder averaged 28.49% w/w, as determined by HPLC (Table 3). This batch of the extract was used throughout this study.

Table 3. Content of tartaric acid in the extract powder

	Sample no.			Average
	1	**2**	**3**	
Content of tartaric acid (%w/w)	28.87	28.57	28.03	28.49 ± 0.43

Effects of types and concentrations of emulsifiers

It is well known that variations in the type of Spans® (e.g. Span® 20, 40, 60, etc.) or Tweens® (e.g. Tweens® 20, 40, 60, etc.) results from variations in the type of fatty acid used. For example, sorbitan monooleate or in trade name Span® 80 are produced by the esterification of one of the hydroxyl groups of sorbitan with oleic acid, and polysorbate 80 or in trade name Tween® 80 contains twenty oxyethylene groups and one oleic acid in the molecule. The variations in the type of fatty acid incorporated in the molecule of Tweens® or Spans® produce a range of products of differing oil and water solubilities. The oil and water-soluble tendencies of these emulsifiers are represented by HLB value. In general, for o/w emulsion, Tweens® are blended with the Spans® to form a film at the oil/water interface, and subsequently provide a stable emulsion. The question is which pairs of the emulsifier blend should be used. From theoretical considerations, the most stable emulsions are formed when both emulsifying agents are of the same fatty acid or of the same hydrocarbon chain length (Schulman and Cockbain, 1940b). For example, the pair of Tween® 80 and Span® 80 should provide the emulsion with more stability than the pair of Tween® 80 and Span® 20. However, it must be realized that in fact partition of some ingredients into the oil phase, and vice versa may occur, and that affects the interfacial film forming. Thus, the stability of the emulsion prepared by relying on the mentioned theory may be out of the expectation.

Our preliminary study demonstrated that the using of the pairs of the nonionic polymers containing the same fatty acid (Tween® 20 + Span® 20, Tween® 60 + Span® 60, Tween® 80 + Span® 80) had provided the coalescence after stability study (data not shown). These results were unexpected and also indicated the possibility of the partition phenomenon occurring in the prepared emulsion system. Therefore, the blends of a given pair of the nonionic emulsifiers with the different length of hydrocarbon chain and/or the same length of hydrocarbon chain but different number of saturated atom in hydrocarbon chain were used instead of as the formulas shown in Table 2, and the physical characteristics and stability of the emulsion obtained from each pair of the emulsifier blend were investigated as shown in Table 4. All formulas provided the o/w emulsion with milky white coloring, smooth texture, low viscosity and pH of 7. The formula composed of the emulsifier blend of Span® 80 and Tween® 60 provided the most stable emulsion whereas the others provided the less stability with the appearance of creaming. In the case of our emulsion system, therefore, the using of the pairs of the same hydrocarbon chain length but the different saturated atom number provided the best stable emulsion.

Generally, the emulsions will only be miscible with liquids that are miscible with its external phase (Friberg *et al*., 1988). Resulting from the dilution test indicated that all prepared emulsions were o/w type because they were miscible with the water added. These findings confirmed our expectation and also indicated that the number of the o:w phase ratio might be used to identify the emulsion types.

Table 4. Physical characteristics and stability of the extract-free emulsion with various pairs of the emulsifier blend consisted of

Characteristic	**Formula**			
	$\mathbf{S_{80}T_{20}}$	$\mathbf{S_{80}T_{60}}$	$\mathbf{S_{40}T_{20}}$	$\mathbf{S_{40}T_{60}}$
White of color	+++	+++	+++	+++
Smoothness of texture	++	+++	+++	+++
Viscosity	+	+	+	+
pH	6	5.5	6	6
Type	o/w	o/w	o/w	o/w
*Creaming	++	-	+	++
*Coalescence	-	-	-	-

Note: The symbols of **+** and - represent the appearance and no appearance, respectively. The number of the symbol of (+) indicates a degree of the appearance (+ to +++). The symbol of *represent the appearance of the creaming or coalescence after the stability test.

Effects of types and concentrations of thickening agents

According to the previous study, the emulsion prepared from the blend between Span® 80 and Tween® 60 (formula of $S_{80}T_{60}$) showed the best stability, including the favorable appearance. However, the viscosity of the emulsion obtained was very low. It has been reported that a direct relationship exists between the viscosity of an emulsion and the viscosity of its external phase whereas. Increase of the viscosity of the external phase can be prepared by gelation of the continuous phase. Such action changes the character of the emulsion from a liquid to a more paste-like consistency and also provides more stable emulsion by reducing the flocculation rate of the emulsion (Florence and Whitehill, 1982, Friberg *et al*., 1988, Garrett, 1965). Thus, the thickening agent including MC 1500 or Carbopol® 940 with various concentrations was incorporated into the external phase of the emulsion to improve its viscosity. The formulas of the emulsions consisting of Carbopol 940 or MC 1500, and their characteristics and stability are shown in Table 5.

In this study we found that the formula with 0.20% of Carbopol® 940 ($S_{80}T_{60}C$) gave the emulsion with good characteristic including viscosity, that was close to the commercial product (Loreal®cleansing lotion clarifying A_3), non-tacky feel and rich buttery texture, and good stability. Methyl cellulose also had an excellent viscosity and clarity, but provided the emulsions with too rigid texture and tacky feel. In this reason, the formula of $S_{80}T_{60}C_{0.2}$ was the final extract-free formula selected for preparing the the emulsion containing the tamarind fruit extract.

Effects of concentrations of AHAs

The formulas of the emulsions containing various concentrations of AHAs are shown in Table 6 and the characteristics and stabilities of those prepared emulsions are shown in Table 7.

Since the tamarind fruit pulp extract was freely soluble in water, this extract was miscible well with the external phase of o/w emulsion and the consequent emulsions obtained from all formulas appeared in Table 6 did not show any sign of incompatibility or precipitation after standing at the room temperature for 1 month. However, stabilizing product containing AHAs may be a problem after long period of storage. This is because ions with high content regarding to acidic property of AHAs may be incompatible with other ingredients consisting in the emulsion formula. Therefore, the accelerated test including the heat-cool cycling method was performed to determine whether or not all prepared emulsions were stable.

In practice, the incompatibility especially between the emulsifiers and/or thickening agent with other components must be avoid because such incompatibility mainly provides the undesirable effects to the emulsion stability and texture. In this study, therefore, the nonionic emulsifiers were employed to minimize the incompatibility phenomenon since they have a greater degree of compatibility with the other ingredients than do anionic or cationic surfactants and are less sensitive to changes in pH (Idson, 1988). Focusing on

Table 5. Formulas of the extract-free emulsion with various kinds and concentrations of thickening agent and the physical characteristics and stability of the emulsions prepared

Component (% w/w)	Formula							
	$S_{80}T_{60}C_{0.2}$	$S_{80}T_{60}C_{0.4}$	$S_{80}T_{60}C_{0.6}$	$S_{80}T_{60}C_{1}$	$S_{80}T_{60}M_{0.2}$	$S_{80}T_{60}M_{0.4}$	$S_{80}T_{60}M_{0.6}$	$S_{80}T_{60}M_{1}$
Oil phase								
Span® 80	1.51	1.51	1.51	1.51	1.51	1.51	1.51	1.51
Isopropyl myristate	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Stearyl alcohol	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Stearic acid	1.50	1.50	1.50	1.50	1.50	1.50	1.50	1.50
Liquid paraffin	3.00	3.00	3.00	3.00	3.00	3.00	3.00	3.00
Water phase								
Tween® 60	5.49	5.49	5.49	5.49	5.49	5.49	5.49	5.49
Propylene glycol	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Glycerin	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00
Disodium EDTA	0.15	0.15	0.15	0.15	0.15	0.15	0.15	0.15
Carbopol® 940	0.20	0.40	0.60	1.00	-	-	-	-
TEA	0.70	0.70	0.70	0.70	-	-	-	-
MC 1500	-	-	-	-	0.20	0.40	0.60	1.00
Methyl paraben	0.20	0.20	0.20	0.20	0.20	0.20	0.20	0.20
Propyl paraben	0.02	0.02	0.02	0.02	0.02	0.02	0.02	0.02
Deionized water added to	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Characteristics								
Color	white	white	white	white	creamy white	creamy white	creamy	creamy
Smoothness of texture	+++	+++	+++	+++	+	+	+	+
Viscosity	++	+++	paste	paste	+++	paste	paste	paste
pH	/	/	7	7	6	6	/	/
Stability								
Creaming/Coalescence	/	/	-	-	-	-	-	-

The symbols of + and - represent the appearance and no appearance, respectively. The number of the symbol of (+) indicates a degree of the appearance (+ to +++). The symbol of / represents unevaluated data.

Table 6. Formulas of emulsions with various concentrations of tamarind fruit pulp extract

Component (% w/w)	Formula		
	$S_{80}T_{60}C_{0.2}E_{0.5}$	$S_{80}T_{60}C_{0.2}E_{1}$	$S_{80}T_{60}C_{0.2}E_{1.4}$
Oil phase			
Span® 80	1.51	1.51	1.51
Isopropyl myristate	5.00	5.00	5.00
Stearyl alcohol	1.00	1.00	1.00
Stearic acid	1.50	1.50	1.50
Liquid paraffin	3.00	3.00	3.00
Water phase			
Tween® 60	5.49	5.49	5.49
Propylene glycol	5.00	5.00	5.00
Glycerin	5.00	5.00	5.00
Disodium EDTA	0.15	0.15	0.15
Carbopol®940	0.20	0.40	0.60
TEA	0.70	0.70	0.70
MC 1500	-	-	-
Tartaric acid (28.5% w/w in the extract powder)	0.50	1.00	1.40
Methyl paraben	0.20	0.20	0.20
Propyl paraben	0.02	0.02	0.02
Deionized water added to	100.00	100.00	100.00

The symbols of + and - represent the appearance and no appearance, respectively. The number of the symbol of (+) indicates a degree of the appearance (+ to +++).

the thickening agent used, it is widely known that Carbopol® polymer is highly water and polar solvent soluble polymer which functions as efficient thickener and stabilizer for emulsions. In addition, it provided the emulsion with the smooth texture and non-tacky feel, according to the results obtained from our former experiment. Carbopol® polymer as supplied is dry and tightly coiled acidic molecules. Once dispersed in water, the molecules begin to hydrate and partially uncoil. The most common way to achieve maximum thickening from Carbopol® polymer is by neutralizing the Carbopol® polymer with a common base such as TEA. Neutralization ionized the Carbopol® polymer, generating negative charges along the polymer backbone. Repulsion of these negative charges causes the molecules to completely uncoil into an extended structure and gives instantaneous thickening emulsion formation. Therefore, the incorporation of the acidic compounds like AHAs into the formula containing the neutralized Carbopol® polymer may affect the viscosity and consequently decrease the stability of the final products. This effect possibly results from decrease in the negative charges in polymer backbone and contribution of residual salts according to the interaction between the negative charges of the neutralized polymer and the positive charges of AHAs. However, in this study we demonstrated that the using of an appropriate concentration of AHAs (0.5% of tartaric acid, formula of $S_{80}T_{60}C_{0.2}E_{0.5}$) together with the using of an appropriate preparation procedure could provided the emulsion with good

Table 7. Physical Characteristics and stabilities of emulsions containing tamarind fruit pulp extract at before and after stability test

Physical characteristics	**Formula**					
	$S_{80}T_{60}C_{0.2}E_{0.5}$		**$S_{80}T_{60}C_{0.2}E_{1}$**		**$S_{80}T_{60}C_{0.2}E_{1.4}$**	
	Before	After	Before	After	Before	After
Color	creamy	creamy	light brown	light brown	light brown	light brown
Smoothness of texture	+++	+++	+++	+++	+++	+++
Viscosity	++	++	++	++	++	++
pH	4.0	4.0	3.6	3.8	3.6	3.6
Creaming	-	-	-	+*	-	+**
Coalescence	-	-	-	-	-	-
Tartaric acid concentration (mean±S.D. of % mg/ml)	0.17± 0.08	0.19± 0.01	0.17± 0.01	0.17± 0.01	0.20± 0.01	0.19± 0.02

The symbols of + and - represent the appearance and no appearance, respectively. The number of the symbol of (+) indicates a degree of the appearance (+ to +++). The symbol of * represents the appearance of creaming after 4 cycles of heat-cool stability test. The symbol of ** represents the appearance of creaming after 3 cycles of heat-cool stability test.

appeal and with good physical and chemical stability, even if both the AHAs and Carbopol® polymer were present in the formula, as shown in Table 7. Viscosity of the prepared emulsion obtained from the formula of $S_{80}T_{60}C_{0.2}E_{0.5}$ was close to viscosity of the commercial product (Loreal®cleansing lotion clarifying A_3), as shown in Fig. 1. Furthermore, there was not significant different in the viscosity of the $S_{80}T_{60}C_{0.2}E_{0.5}$ emulsion between at before and after stability test. These findings also indicated the good stability of the emulsion system prepared. In preparation process of the emulsion containing the extract, the Carbopol® was neutralized by adding an appropriate amount of TEA after the aqueous solution of the extract was added in the preformed emulsion. This process was performed to avoid the direct and/or vigorous ionic interaction between the negative charges of the neutralized polymer and the AHAs and consequently provided the emulsion with good stability. However, we found that the decrease in the stability of the prepared emulsion was proportional to the increase in pH of the final product and the amount of AHAs incorporated. This might result from a higher concentration of the residual salt upon the neutralized Carbopol® at a higher concentration of ions generating from acidic AHAs. Such higher concentration of the residual ions, coupled with lower amount of the neutralized polymer led to lower viscosity and consequently lower stability of the emulsion.

The final product with 0.5% of tartaric acids also provided the emulsion with pH of 4 that was close to the normal pH range of the skin (4.5 to 5.5) (Abe *et al*., 1980) and could maintain AHAS activity. Generally, a low pH is required for maximal AHA activity (Greaves, 1990). At low pH (2 to 3) even small

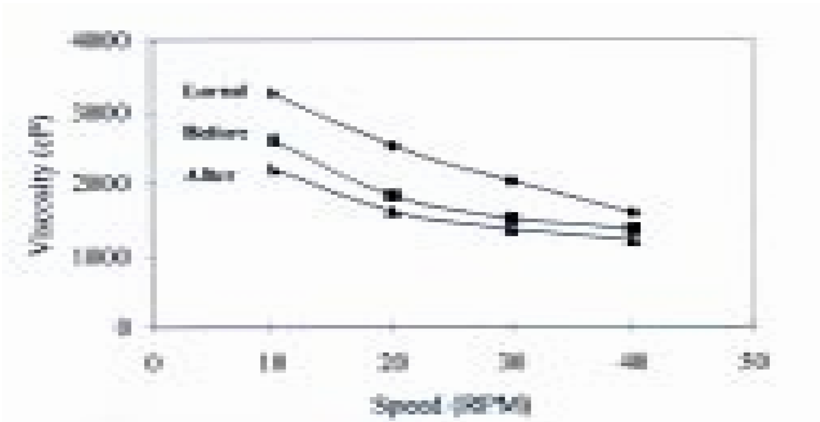

Figure 1. Viscosity of the emulsion containing the extract at before and after stability test and viscosity of the commercial emulsion product (Loreal®cleansing lotion clarifying A_3).

concentrations of AHAs can be effective because a major amount of the AHAs is available. However, it has been recommended that the pH of the formulation should not be above 4 to maintain AHAs activity and avoid irritation to skin (Smith, 1994).

Conclusion

In this study, we formulated and developed o/w emulsion containing the natural AHAs derived from tamarind fruit pulp for application in facial skin cleansing. The aqueous solution of the crude extract was lyophilized, and the content of tartaric acid in the obtained extract powder was determined by using HPLC. The physical characteristics and stability of the prepared products were the major criteria in this study to determine the suitable formula for application in the facial skin cleansing. We demonstrated that the final product with the extract in amount of corresponding to 0.5% of tartaric acid showed the good physical characteristics and stability and also provided the desirable pH. However, the further studies such as irritability to skin, skin cleansing efficiency, and acceptance from the consumer have to be performed to evaluate the valuable of our product for the cosmetic market.

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