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STUDY ON THE STABILITY OF O/W AND MLV EMULSION CONTAINING DIHYDROXYACETONE

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Summary :

Dihydroxyacetone (DHA) has been used as a self tanning agent and many emulsion formulations containing DHA have been studied. In an emulsion, many factors which have negative effect on DHA and the resultant DHA decomposition can destabilize the emulsion base. In this study, two kinds of emulsion with 5% DHA were prepared, O/W type emulsion and Multilamellavesicle (MLV) type emulsion to compare the stabilization effects of both emulsions on the DHA. The DHA concentration was analyzed quantitatively by high performance liquid Chromatography (HPLC), also the pH and viscosity of both emulsions were measured for stability. This process was carried out over 4 months. For HPLC, a bondaclone C_{18} column with a mobile phase of distilled water and UV detector were used. The results of these experiment showed that DHA is more stable in an MLV emulsion than it is in an O/W type emulsion.

Key Words : Dihydroxyacetone (DHA), Multilamellavesicle (MLV), stabilization, HPLC

Introduction

The most important active substance which tans skin by external application is DHA, the tanning mechanism is a Maillard reaction which takes place between DHA and the amines of the Stratum Corneum. The brown coloring appears after a reaction time of at least 2 hours. This tan is substantive, but fades as the upper layers of the epithermis wear away.[1,2,3] DHA can be used in various cosmetic formulations, emulsions of the O/W and W/O types, aqueous lotions and gels are appropriate for this purpose.[4] The concentration of DHA in tanning products lies in the range from 2 to 5%. In order to obtain good DHA stability in the final preparation, certain basic aspects have to be considered when tanning products are developed. DHA is stable between pH values of 4 and 6. When the pH rise above 7, brown colored compounds are formed after isomerization and condensation, which lead to loss of efficacy.[2,5] Furthermore, the following factors have a negative

effect on DHA: heat, microorganisms, all kinds of compounds containing nitrogen, oxygen/oxidizing compounds, UV light and perfume oils/extracts.[5] In an emulsion, DHA can be decomposed by heat, microorganisms, UV light and such decomposition can destabilized the emulsion base. The microbiological decomposition reactions are often characterized by an accompanying pungent smell, caused by the formation of various organic acids and aldehydes.[6,7,8] For the determination of DHA in an emulsion, Gas chromatography (GC), HPLC, Thin layer chromatography (TLC) and enzymatic methods are all useful. HPLC is less sensitive than GC, but detects all isomerization, decomposition products. For HPLC, a C_{18} column with mobile phase of water and refractometer detector or UV detector were used.[2,5,9,10] In this experiment, O/W type emulsion and MLV type emulsion were prepared to compare the stabilizing effects of the DHA. Natural or synthesized lipids make good MLV which is composed of stable amphiphilic moleculars.[11] Liposomes are vesicles that form when phospholipids swell and hydrate in the presence of an aqueous phase. The vesicular structure of liposomes can be stabilized by cholesterol. An ionic charge incorporated in the lamellar vesicular structures may improve physical stability. MLV was prepared by Bangham, consisting of concentric spheres of bilayers. Recently microfluidizer has been used to produce liposomes of a defined size distribution.[12]

Materials and Methods

1. Materials

1-1 O/W emulsion formulation		1-2 MLV emulsion formulation	
Stearic acid	2.00	Cholesterol	5.00
Cetyl alcohol	1.50	Sitosterol	5.00
Paraffin oil liquid	7.00	Polyoxyethylene Alkyl ether	1.00
Squalane	4.00	Paraffin oil liquid	10.00
Sorbitan oleate	2.00	Propylene Glycol	5.00
Glyceryl stearate	1.00	Carbomer	0.3
Propylene Glycon	5.00	TEA	0.3
Carbomer	0.30	DHA(Merck. Co.)	5.00
TEA	0.30	Methyl paraben	0.10
DHA(Merck. Co,)	5.00	Pure water	
Methyl paraben	0.10		
Pure water			

2. Methods

2-1. HPLC condition

HPLC - Waters model 441 UV/vis detector (280nm)
510 Pump
U6K Injector
Column - Bondaclone C18
Mobile phase : 100% Pure water
Injection Volume : 10 ml flow rate : 1 ml/min
Temperature : ambient running time: 10 minutes

2-2. Sample extraction

Both emulsions were diluted with pure water and the solutions were shaken by vortex mixer for 30min. After the first filtration through filter paper, a 0.45 membrane filter was used for the second filtration and the filtered solutions were injected.

2-3. pH measurement

pH meter - Mettler delta 340
Temperature 25 C

2-4. Viscosity measurement

viscometer - Brookfield RVT viscometer
Spindle - N0.6
RPM - 50
temparature - 25

Results

1. The analysis of DHA

DHA in both emulsions was analyzed by HPLC with a bondaclone C_{18} column and mobile phase of distilled water for good eluent. The result of scanning for optimal wavelength was 280nm and the retention time of DHA under these conditions was 3.25 min. Fig.1, Fig. 2, Fig. 3 give the chromatograms of DHA in standard solution, O/W emulsion solution and MLV solution.

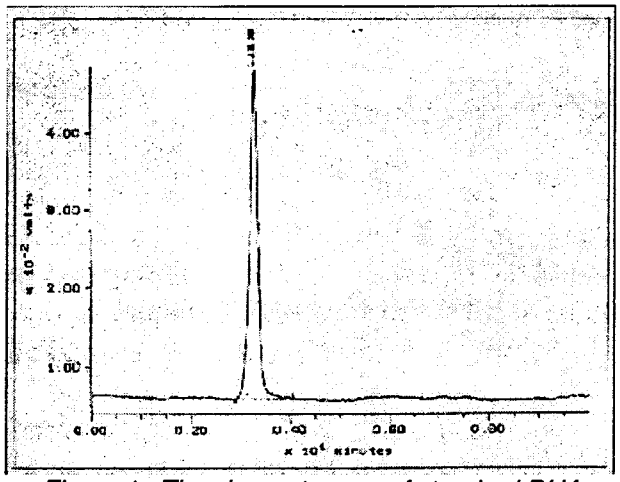

Figure 1. The chromatagram of standard DHA

(Figures 2 and 3 are not available)

2. The change of DHA concentration

The concentration of DHA in both emulsions was checked at intervals of fifteen days for 4 months. After the first month, the decrease of DHA concentration in O/W emulsion was 0.011% and in MLV emulsion it was 0.005%. Considering that the initial total concentration of DHA in the emulsion bases was 5%, the difference between both emulsions was not noticeable. DHA in O/W emulsion decomposed quickly from the second month, after 60 days the DHA percentage had decreased by 0.514%, after 90 days 1.185%, 1.512% of DHA decomposed after 4 months. Whereas the decrease of DHA concentration in MLV emulsion was 0.331% after 4 months. Table 1 and Fig.4 show the result of this experiment

Emulsion		1days	15days	30days	45days	60days	75days	90days	105days	120days
O/W	concentration(%)	5.000	4.989	4.932	4.719	4.486	4.125	3.815	3.687	3.488
	percentage of decrease	-	0.22	1.36	5.62	10.28	17.50	23.70	26.26	30.24
MLV	concentration(%)	5.000	4.995	4.988	4.969	4.936	4.914	4.887	4.786	4.669
	percentage of decrease	-	0.11	0.25	0.62	1.28	1.72	2.26	4.28	6.62

Table 1. The change of DHA concentration

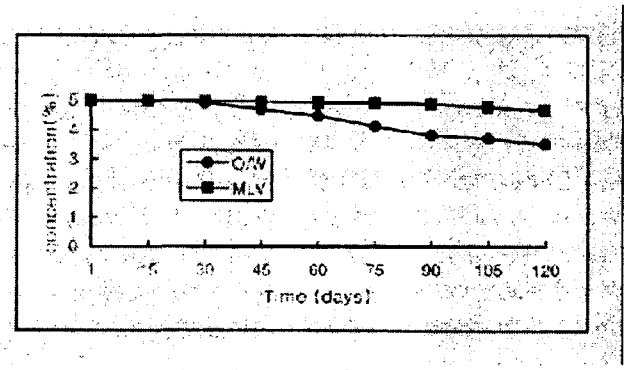

Figure 4. The change of DHA concentration

3. The change of pH and viscosity

The pH and viscosity of both emulsions were measured at the same intervals as the DHA concentration was analyzed. The pH and viscosity of both emulsions diminished proportionally to the reduction in DHA concentration. When the emulsion bases were made, the pH of the MLV emulsion and the O/W emulsion were 5.82 and respectively 5.68. After 4months, there was large difference, the pH of the MLV emulsion was 5.65, and the pH of O/W emulsion was 4.12. As the pH of both emulsions had diminished, the viscosity reduced inevitably. The viscosity of the O/W emulsion was decreased from 5,400 to 3,100, whereas the viscosity of the MLV emulsion was decreased from 5,200 to 4,600. Table 2 and Fig. 5, Fig. 6, show the results.

Emulsion		1 day	15days	30days	45days	60days	75days	90days	105days	120days
pH	O/W	5.68	5.60	5.39	5.12	4.91	4.64	4.37	4.30	4.12
	MLV	5.82	5.79	5.78	5.75	5.73	5.74	5.71	5.67	5.65
Viscosity	O/W	5400	5300	5000	4700	4300	3900	3400	3200	3100
	MLV	5200	5200	5100	5000	4800	4800	4800	4600	4600

Table 2. The changes of pH and viscosity

(Figures 5 and 6 are not available)

Discussion .

DHA can be decomposed by many factors in cosmetic formulations. To maintain the stability of DHA in an emulsion, two kinds of emulsions were formulated, one was O/W type emulsion and the other was MLV type emulsion. Both emulsions were compared, for their stabilization effect on DHA and the change in DHA concentrations was analyzed quantitatively by HPLC. After 4 months, the DHA concentration in the O/W emulsion had decreased from 5.00% to 3.488% and in the MLV emulsion it had decreased from 5.00% to 4.669%. Moreover, the pH and viscosity were measured to

compare the stability of both emulsion bases. The experiment yielded the following results: the pH of O/W emulsion decreased from 5.68 to 4.12, whereas the pH of MLV emulsion decreased from 5.82 to 5.68. The viscosity of the O/W emulsion decreased from 5,400 cps to 3,100 cps, while the viscosity of the MLV emulsion decreased from 5,200 to 4,600. These results showed that DHA is more stable in a MLV emulsion than it is in an O/W type emulsion. In the O/W emulsion DHA decreased by 1.5% which means that 30% of the total DHA percentage was isomerized or had decomposed. When DHA is decomposed by microorganisms in aqueous solution, various organic acids and aldehydes can be produced which lead to low pH and viscosity. Low pH can influence the carbomer chains. Our conclusion is that an MLV type emulsion is better for the stabilization of DHA in an emulsion, compared with an O/W type emulsion.

References

1. V Usdin, Cosm & Toil 91 29 (1976)

2. T Kurz, Cosm & Toil 109 55 (1994)

3. M Rieger, Cosm & Toil 98 47 (1983)

4. T Kurz, Parfumerie und Kosmetik 77 550 (1996)

5. Bobin M, Farmaco 38 415 (1983)

6. Goldman L, J. of the Society of Cosmetic Chemists, 163 (1960)

7. HG Lento, Food Res. 25 750 (1960)

8. Ind. Eng. Chem. Res. 6 36 (1997)

9. Bobin M, Farmaco 38 403 (1983)

10. Baruffini A, Farmaco 36 424 (1981)

11. Hans E, Cosm & Toil 106 45 (1991)

12. Eric M, Pharmaceutical Manufacturing 2(8) 18 (1985)