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Note

Determination of sunscreen agents in cosmetic products by reversed-phase high-performance liquid chromatography

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Cosmetic products containing sunscreen agents are widely available. Sunscreen agents are used to protect the skin against sunburn and to prevent the degradation of cosmetic products by sunlight. However, the regular application of these products may cause irritation and allergic or photoallergic contact dermatitis^{1,2}. In order to ascertain which sunscreen agents are present in commercial cosmetic products and to prevent undesirable side-effects, simple and reliable methods for the simultaneous determination of sunscreen agents are required.

A few methods have been proposed for the identification and determination of sunscreen agents in cosmetic products, based on gas-liquid chromatography³ and high-performance liquid chromatography (HPLC)^{4–9}. Cumpelik³ determined 2-ethoxyethyl 3-(4-methoxyphenyl)-2-propenoate (Cinoxate), 2-ethylhexyl 4-(dimethylamino)benzoate (Escalol 507) and 2-ethylhexyl 3-(4-methoxyphenyl)-2-propenoate (Parsol MCX) by temperature-programmed gas chromatography after silanization. Gagliardi *et al.*⁷ assayed (2-hydroxy-4-methoxyphenyl)phenylmethanone (Oxybenzone), Escalol 507, 1-[4-(1,1-dimethylethyl)phenyl]-3-(4-methoxyphenyl)-1,3-propanedione (Parsol 1789) and Parsol MCX by HPLC. These procedures are relatively time consuming and laborious because of the complex sample pretreatment and extraction steps required, and therefore are not suitable for the routine analysis of cosmetic products.

In this paper we describe a reversed-phase HPLC method for the rapid and simultaneous determination of six sunscreen agents {Cinoxate, Oxybenzone, 1-[4-(1-methylethyl)phenyl]-3-phenyl-1,3-propanedione (Eusolex 8020), Escalol 507, Parsol 1789 and Parsol MCX} in cosmetic products involving a simple extraction for sample preparation.

EXPERIMENTAL

Reagents and materials

The following materials and reagents were used: Cinoxate (Givaudan, courtesy of Kokuritu Eisei Shikenjo, Tokyo, Japan), Oxybenzone (Tokyo Kasei Kogyo, Tokyo, Japan), Eusolex 8020 (Merck, courtesy of Kanto Chemical, Tokyo, Japan), Escalol 507 (Van Dyk, courtesy of Ina Trading, Tokyo, Japan), Parsol 1789 and

Parsol MCX (Givaudan, Tokyo, Japan). All other chemicals were of HPLC grade. Water was deionized and distilled from glass apparatus. All solvents and solutions for HPLC analysis were filtered through an FR-40 Fuji Film Micro Filter (pore size 0.4 μm) and vacuum degassed by sonication before use.

Standard solutions

Stock solutions of standards were prepared by dissolving the appropriate amount of sunscreen agent in tetrahydrofuran (THF). A set of standard solutions were produced by diluting aliquots of the stock solutions with THF to 50 ml in volumetric flasks. The concentrations of each compound for the calibration graphs ranged from 1 to 10 $\mu\text{g}/\text{ml}$ and from 10 to 100 $\mu\text{g}/\text{ml}$.

Sample solutions

Taking into account the content of sunscreen agents in the cosmetic products, about 0.05–5.0 g of the latter were weighed accurately in a 50-ml beaker, diluted to about 20-ml with THF, dissolved by sonication and transferred into a 50-ml volumetric flask. The beaker was rinsed twice with 5-ml portions of THF and the rinsings were combined in the volumetric flask. The solution was diluted to volume with THF. An aliquot of the solution was filtered through a 0.4 μm membrane filter prior to HPLC analysis.

High-performance liquid chromatography

The HPLC system consisted of a Model 665A-12 pump (Hitachi, Tokyo, Japan), a Model 7125 injector equipped with a 20 μl sample loop (Rheodyne, Cotati, CA, U.S.A.) and a Model 665A-21 variable-wavelength UV detector (Hitachi). Chromatograms and peak areas were obtained with a Model 883A reporting integrator (Hitachi). A TSKgel ODS-80T_M (particle size 5 μm , 15 cm \times 4.6 mm I.D.; TOSOH, Tokyo, Japan) analytical column was used at 40°C. The mobile phase was methanol–THF–water (4:6:6) at a flow-rate of 1.0 ml/min. The UV detector was operated at 325 nm with a sensitivity of 0.04 a.u.f.s.

By means of the injection valve, 5 μl of the prepared sample solution and standard solution were chromatographed under the operating conditions described above. Quantitation was based on the peak area of the sample.

RESULTS AND DISCUSSION

Fig. 1 shows the UV spectrum of the sunscreen agents in ethanol. The absorbance maxima for Cinoxate, Oxybenzone, Escalol 507, Eusolex 8020, Parsol 1789 and Parsol MCX are 302, 286 (second maxima at 325 nm), 309, 345, 358 and 308 nm, respectively. However, UV monitoring with the absorbance maxima could not be used because it was required to determine these compounds simultaneously. As the absorbances of the individual sunscreen agents were similar from 320 to 330 nm, as shown in Fig. 1, the UV monitoring wavelength was selected as 325 nm.

Fig. 2 shows the chromatogram of a standard mixture of sunscreen agents. Six sunscreen agents were eluted as fairly symmetrical peaks, well resolved from each other. Gagliardi *et al.*⁷ reported that Escalol 507, Parsol 1789 and Parsol MCX were eluted almost at the same time on a reversed-phase ODS column using a mobile phase

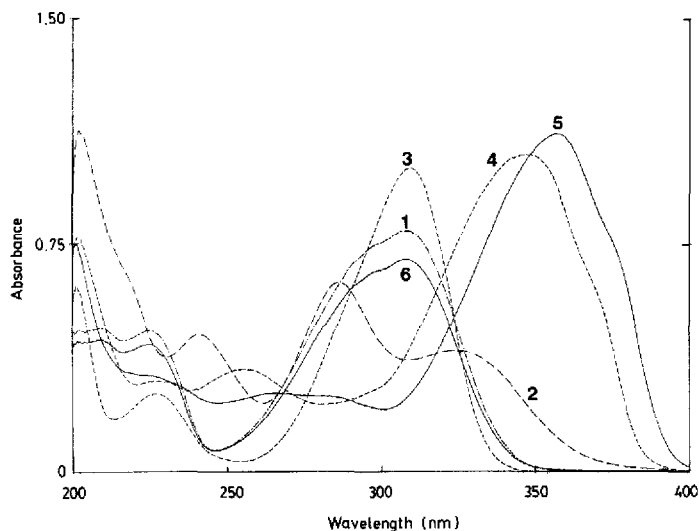


Fig. 1. Absorption spectrum of sunscreen agents. Conditions: cell length, 1 cm; concentration, 10 mg/l. 1 = Cinoxate; 2 = Oxybenzone; 3 = Escalol 507; 4 = Eusolex 8020; 5 = Parsol 1789; 6 = Parsol MCX.

system with an ion-pair partition process. Under our chromatographic conditions, good separation among Escalol 507, Parsol 1789 and Parsol MCX was achieved using methanol-THF-water (4:6:6) as the mobile phase.

Calibration graphs were constructed by plotting the peak area vs. the concentration of standard injected. Good linearity over the ranges 1–10 $\mu\text{g/ml}$ and 10–100 $\mu\text{g/ml}$ for each sunscreen agent was obtained; the plots passed through the origin.

Recovery tests were carried out on cosmetic products for the evaluation of the reproducibility and accuracy of the proposed method. Six cosmetic products were

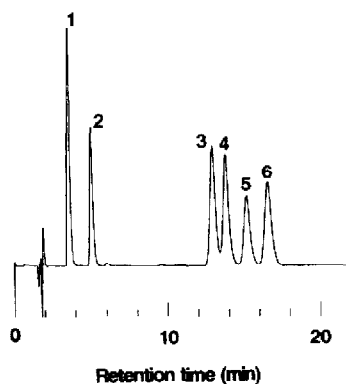


Fig. 2. Liquid chromatogram of sunscreen agents. Conditions: column, TSKgel ODS-80T_M (150 mm \times 4.6 mm I.D.); eluent, methanol-THF-water (4:6:6); flow-rate, 1.0 ml/min; column temperature, 40°C; injection volume, 5 μl . Peaks: 1 = Cinoxate; 2 = Oxybenzone; 3 = Escalol 507; 4 = Eusolex 8020; 5 = Parsol 1789; 6 = Parsol MCX.

TABLE I
RECOVERIES OF SUNSCREEN AGENTS FROM COSMETICS

The amounts of standard samples added were as follows: suntan, 1–2% (w/w); foundation, 1% (w/w); lipstick, 1% (w/w); hair rinse, 0.2% (w/w); milk lotion, 0.1% (w/w); lotion, 0.1% (w/w). C.V. = coefficient of variation ($n = 3$).

<i>Cosmetic</i>	<i>Cinoxate</i>		<i>Oxybenzone</i>		<i>Escalol 507</i>	
	<i>Recovery (%)</i>	<i>C.V. (%)</i>	<i>Recovery (%)</i>	<i>C.V. (%)</i>	<i>Recovery</i>	<i>C.V. (%)</i>
Suntan	98.3	1.3	100.2	2.8	99.5	3.7
Foundation	101.2	1.7	99.1	1.5	96.7	0.7
Lipstick	104.4	3.4	100.9	3.2	100.4	1.4
Hair rinse	98.3	1.3	98.1	0.8	97.0	2.5
Milk lotion	97.1	2.4	98.1	2.2	98.7	1.3
Lotion	97.2	1.6	99.6	2.7	100.9	2.3
	<i>Eusolex 8020</i>		<i>Parsol 1789</i>		<i>Parsol MCX</i>	
	<i>Recovery (%)</i>	<i>C.V. (%)</i>	<i>Recovery (%)</i>	<i>C.V. (%)</i>	<i>Recovery (%)</i>	<i>C.V. (%)</i>
Suntan	99.0	2.0	97.3	0.9	99.9	0.7
Foundation	92.4	0.5	93.6	0.9	99.9	1.2
Lipstick	100.2	1.6	99.5	2.0	102.3	1.3
Hair rinse	97.4	2.2	97.3	0.4	99.8	0.4
Milk lotion	100.0	1.0	99.0	1.0	97.5	0.2
Lotion	98.3	2.2	98.7	1.5	98.6	0.9

spiked with the amounts of the agents reported in Table I and subjected to the whole procedure. As shown in Table I, excellent recoveries and precision were observed.

The proposed method was applied to the determination of sunscreen agents in 33 samples of commercial cosmetic products. The results obtained are shown in Table II. None of the cosmetic products contained Eusolex 8020. Foundations, lipsticks, hair tonics and shampoos contained one of the sunscreen agents investigated; suntans and milk lotions contained a combination of two or three of Oxybenzone, Escalol 507

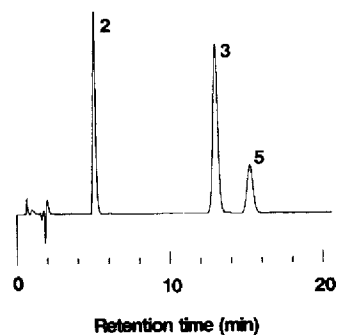


Fig. 3. Liquid chromatogram of sunscreen agents in a commercial milk lotion. Peaks: 2 = Oxybenzone; 3 = Escalol 507; 5 = Parsol 1789.

and Parsol 1789. Several cosmetic products contained less than 0.1% of the sunscreen agents. In such instances, it is concluded that the sunscreen agents are used to prevent the degradation of the cosmetic products. Fig. 3 shows a typical chromatogram for a milk lotion. The peaks of the sunscreen agents did not suffer interference from other cosmetic ingredient in any of the samples examined.

In conclusion, the proposed method is useful for the simultaneous determination of six sunscreen agents in cosmetics products. This method is very simple, precise and accurate, and is suitable for the routine analysis of cosmetics.

TABLE II
CONTENTS OF SUNSCREEN AGENTS IN COSMETICS

Sample	No.	Concentration (% w/w)				
		Cinoxate	Oxybenzone	Escalol 507	Parsol 1789	Parsol MCX
Suntan	1		2.6	6.7		
	2		4.3	8.8		2.4
	3		3.0	3.4		
	4		0.7	3.8		
	5		0.39	3.6		
Foundation	1			2.9		
	2				0.0091 ^a	
	3			0.45		
	4			0.68	0.49	
	5				0.0031 ^a	
	6	0.20				
	7			4.2		
	8			0.10		
	9					2.2
	10					1.5
	11					3.0
Lipstick	1					1.1
	2		2.9			
	3					2.2
Milk lotion	1		0.10	0.10	0.033	
	2		0.10	0.10	0.053	
	3		0.051			
Lotion and hair tonic	1	0.10				
	2					0.023
	3		0.0093 ^a			
	4		0.020			
	5		0.099			
	6		0.048			
Hair rinse and shampoo	1			0.17		
	2			0.0081 ^a		
	3		0.10			
	4		0.010 ^a			
	5		0.10			

^a The range of the calibration graph used was 1–10 µg/ml.

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