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Note

Determination of aromatic alcohols in cosmetic products using reversed-phase high-performance liquid chromatography

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In the manufacture of cosmetics some aromatic alcohols are used as preservatives. European Economic Community (EEC) Instruction No. 82/368 (enclosure VI) lists the preservatives provisionally authorized for use in cosmetics and their tolerated concentrations.

A number of techniques have been developed for detecting and identifying preservatives in cosmetic preparations and a brief survey of this work has been published[1]. In particular, thin-layer chromatography (TLC)[2–6], gas–liquid chromatography (GLC)[5,6], gel electrophoresis and microbiological methods[7] have been used.

The microbiological assays are non-specific and give only an indication of the nature of the preservatives. The others fail to determine volatile substances such as low-molecular-weight alcohols because they can be lost from the plate as in TLC or masked under the solvent front as in GLC. Considering the characteristics of aromatic alcohols, high-performance liquid chromatography (HPLC) seems to be the most appropriate method for their separation, identification and quantification. In this study we investigated the suitability of HPLC for this purpose.

The aromatic alcohols considered, together with the maximum limits in compliance with the EEC legislation, were as follows: benzyl alcohol (I), 1%; 2-phenoxyethanol (II), 1%; 1-phenoxy-2-propanol (III), 1%; 3,4-dichlorophenylmethanol (IV), 0.15%; and 2,4-dichlorophenylmethanol (V), 0.15%.

The compounds were analysed on an RP-18 column using ethyl 4-hydroxybenzoate as an internal standard (I.S.), acetonitrile in water as the mobile phase and detection at 230 nm. Moreover, the method has been applied successfully to determine all the alcohols in skin cosmetics, shampoos and bath preparations.

EXPERIMENTAL

Reagents

All the alcohols were of analytical-reagent grade and were used as received. I was obtained from Farmitalia-Carlo Erba, II from Merck, III from Pfaltz and Bauer, IV from ICN Pharmaceuticals and V from Boots. The reagents used were HPLC-grade methanol and acetonitrile (Farmitalia-Carlo Erba) and 2 *M* sulphuric acid.

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Water was deionized and doubly distilled in glass. All solvents and solutions were filtered through a Millipore filter (0.5 μm) and vacuum degassed by sonication before use.

Apparatus

A Varian Model 5000 liquid chromatograph equipped with a variable-wavelength UV detector (Varichrom UV 50), a Valco AH60 injection valve and a Waters Assoc. Model 730 integrator–recorder were used. The separations were performed on columns of 5 μm LiChrosorb RP-18 (Merck) (250 × 4.6 mm I.D.).

HPLC conditions

The operating conditions were as follows: mobile phase, acetonitrile–water (10:90) with a linear gradient elution up to 45% acetonitrile in 40 min; flow-rate, 1 ml/min; column temperature, 35°C; injection volume, 10 μl; detector wavelength, 230 nm; and detector sensitivity, 0.32 a.u.f.s.

Calibration graphs

Calibration graphs were prepared by dissolving known amounts of I–V in acetonitrile–water (1:1) containing 85 μg/ml of the I.S. These solutions were processed using the HPLC conditions described above. The ratios of the peak areas of I–V to I.S. were used to calculate the calibration graphs, the slopes of which were used in the quantification of the alcohols in cosmetic products.

Extraction procedure

For each analysis 1 g of cosmetic product was accurately weighed into a glass centrifuge tube, 0.25 ml of 2 *M* sulphuric acid and 3 ml of methanol were added and the tubes were soaked in an ultrasonic bath for 30 min. When the cosmetic sample contained fat-soluble excipients the mixture had to be heated in a water-bath at 60°C for 10 min to break the emulsion, followed by the ultrasonic treatment. The tubes were then centrifuged for 10 min at 900 *g* and the supernatant was transferred into another series of clean glass tubes. The extraction procedure was repeated another time, to the combined extracts was added 1 ml of methanol containing 8.5 mg of the I.S. and the volume was made up to 100 ml with methanol.

RESULTS AND DISCUSSION

The chromatogram obtained on analysis of a standard mixture of I–V is shown in Fig. 1; good resolution of the aromatic alcohols and the I.S. has been achieved.

Table I reports the chromatographic properties of the preservatives examined and their response factors relative to the I.S., calculated from the weight ratios. Under the chromatographic conditions used the retention times was fairly reproducible. The calibration graphs for each preservative were constructed from six consecutive injections; the resulting mean coefficient of variation was less than 2.0%. Linearity was observed up to 20 μg injected for I and up to 6 μg injected for II–V.

To test the applicability of the HPLC method to the assay of aromatic alcohols in cosmetics, five kinds of cosmetic products, including creams, cleansing lotions, shampoos and bath preparations, were studied. To each cosmetic sample, a mixture

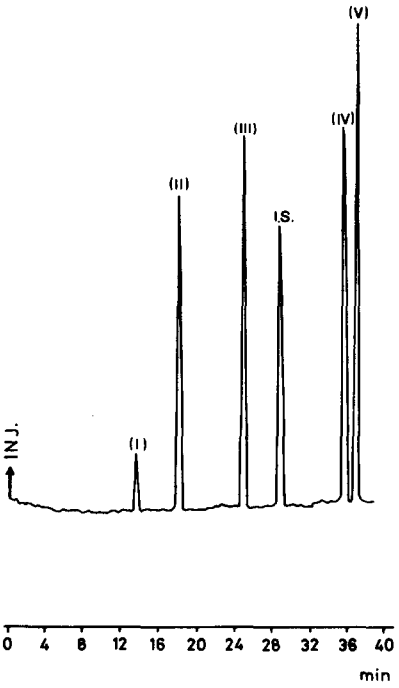

Fig. 1. Typical chromatogram of a standard mixture of aromatic alcohols and I.S. Chromatographic conditions as reported in the text.

of the preservatives under examination was added at the concentrations reported in Table II, which also shows the results obtained. Quantitative recoveries and excellent precision are observed.

Because of its simplicity, selectivity, good recovery and precision, the HPLC assay described here seems suitable for the analysis of aromatic alcohols added as preservatives to different kinds of cosmetic products, particularly to verify their compliance with EEC legislation.

TABLE I

RETENTION TIMES, CAPACITY FACTORS AND RESPONSE FACTORS OF AROMATIC ALCOHOLS

Each value is the mean of five determinations.

Compound	*Retention time (min)*	*Capacity factor*	*Response factor*
I	12.50	5.25	0.015
II	17.17	7.58	0.330
III	24.50	11.25	0.430
I.S.	28.50	13.25	1.000
IV	35.33	16.67	1.020
V	36.33	17.17	1.190

TABLE II

RECOVERY OF AROMATIC ALCOHOLS IN COSMETIC PRODUCTS

Compound	*Night cream*		*Day cream*		*Cleansing lotion*		*Bath foam*		*Shampoo*	
	*A**	*B***	*A**	*B***	*A**	*B***	*A**	*B***	*A**	*B***
I	1.00	96.2 ± 1.9	1.00	93.4 ± 1.6	1.00	92.3 ± 2.0	1.00	91.4 ± 1.5	1.00	96.2 ± 2.1
II	0.30	94.2 ± 1.6	0.30	91.7 ± 1.4	0.30	91.4 ± 2.1	0.30	96.3 ± 1.8	0.30	92.6 ± 1.8
III	0.30	96.3 ± 1.9	0.30	92.3 ± 2.0	0.30	90.6 ± 1.7	0.30	95.4 ± 1.8	0.30	96.4 ± 1.3
IV	0.15	91.4 ± 1.8	0.15	98.2 ± 1.7	0.15	97.6 ± 1.9	0.15	93.2 ± 2.0	0.15	94.5 ± 1.9
V	0.15	93.2 ± 1.5	0.15	100.2 ± 1.7	0.15	100.4 ± 1.4	0.15	101.2 ± 1.3	0.15	98.6 ± 1.6

* Grams added to 100 g of cosmetic sample.

** Recovery (%) ± S.D. (each value is the mean of five determinations).

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