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Investigation of parabens in commercial cosmetics for children in Beijing, China

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Synopsis

Parabens are one of the most common preservatives in cosmetics. Because allergenicity and cytotoxicity potential values are major aspects of preservative safety and parabens are xenoestrogens, safety levels of parabens have been restricted in "Hygienic Standard for Cosmetics" (2007 edition) by the Ministry of Public Health of China, and a high-performance liquid chromatography (HPLC) for the simultaneous determination of parabens is recommended. To investigate whether the commonly used parabens in children's cosmetics were at a safety level, 105 cosmetics for children were randomly purchased from the local market in Beijing and analyzed by the proposed HPLC method. The detection rate of methylparaben was the highest and the next was propylparaben. Among the 105 samples, two or more kinds of parabens were detected in 72 samples with concentrations ranging from 0.02% to 0.75%; 18 samples contained one kind of paraben with concentrations ranging from 0.002% to 0.06%. In this study, the contents of parabens in the 105 samples were all below the restricted levels.

INTRODUCTION

Parabens are preservatives added to cosmetic products for the primary purpose of inhibiting the development of microorganisms. Four parabens (methylparaben, ethylparaben, propylparaben, and butylparaben) were the most frequently used preservatives based on the data from the Voluntary Cosmetic Registration Program (1–4). Although the Cosmetic Ingredient Review Expert Panel support the safety of cosmetic products in which paraben preservatives are used (5), experiments have shown that parabens exhibited an estrogen-like property *in vivo* in an immature rat model, which expanded the current understanding of the potential adverse effects of parabens associated with their estrogen-like activities. Further investigation is needed to elucidate in greater detail the adverse effects of parabens in humans and wildlife (6). Although the endocrine-disrupting bioactivity of parabens is weakly estrogenic, exposure to multiple parabens at low concentrations may increase their synergistic estrogenic activities in rat pituitary lactosomatotrophic GH3 cells through a progesterone receptor-mediated pathway (7). Taking into account

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parabens potential adverse effects, the Ministry of Public Health of China set safety levels at 0.4% (acid) for monoester and 0.8% (acid) for mixed esters (8). The types and contents of cosmetics preservatives in Guangdong Province, China, have been investigated (3). The contents of methylparaben, propylparaben, and butylparaben were all below the restricted levels. However, the concentration of ethylparaben was found to be 2%, which far exceeded the restricted level of 0.4% (3). In contrast, a similar investigation of cosmetics preservatives in Shenzhen City showed that none of the parabens' content exceeded the restricted levels (4).

To the best of our knowledge, no investigation on the contents and parabens frequency in cosmetics for children has been reported in China yet. We believe such an investigation is critical since children are especially vulnerable to parabens' exposure given their skin characteristics. The aims of this study are twofold: First, to study whether the commonly used four parabens in children's cosmetics were below safety level, and second, to evaluate the possible exposure of infants and children to parabens from cosmetic products.

EXPERIMENTAL SECTION

SAMPLES SOURCE

A total of 105 children's cosmetics samples produced from January 2009 to December 2010 were randomly purchased from the local market in Beijing (Table I).

All cosmetic samples were divided into two categories: leave-on products, which were applied to the skin and then intended to remain on the skin (cream, lotion, etc.), and rinse-off products, which were washed off immediately after use (shampoo, shower, etc.).

DETERMINATION METHOD

Parabens were determined by the recommended high-performance liquid chromatography (HPLC) method (5).

Table I
Investigated Cosmetics and the Geological Distribution of the Manufacturers

Country or district	Leave-on products	Rinse-off products	Total
Beijing	24	11	35
Shanghai	23	8	31
Tianjin	8	3	11
Guangdong	9	2	11
Zhejiang	3	—	3
Fujian	—	2	2
America	1	9	10
France	1	—	1
Australia	1	—	1
Total	70	35	105

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Sample pretreatment. An accurately weighed 1.00 g of cosmetic sample was transferred into a 10-ml glass centrifuge tube with plug. The sample was mixed with 10-ml methanol and subjected to ultrasound for 10 min. The solution was then centrifuged at 12,000 rpm for 5 min. The supernatant was filtered through 0.45 μm nylon membrane and then used for HPLC analysis.

HPLC analysis. A Waters 2695-996 HPLC system (Milford, MA) equipped with a 600 gradient pump was used. A Waters Empower software workstation for instrument control as well as data acquisition and processing was applied.

An analytical column of Inertsil® ODS-3 C_{18} (250 × 4.6 mm, 5 μm) from Dikma (GL Science Inc. Tokyo, Japan) was used at room temperature. The mobile phase was a mixture of V(A):V(methanol):V(acetonitrile) = 50:35:15 (where A was 0.05 mol/l sodium dihydrogen phosphate and 2 mmol/l cetyltrimethylammonium chloride, pH 3.5 adjusted with 85% orthophosphoric acid). The flow rate was 1.5 ml/min. A Waters 996 photodiode array detector was used, and the detection wavelength was set at 254 nm. The injection volume of the standard and sample solutions was 10 μl. They were injected by a Waters 717 plus autosampler.

RESULTS AND DISCUSSION

FREQUENCY OF USE OF PRESERVATIVES IN COSMETICS FOR CHILDREN

In this study, four parabens (methylparaben, ethylparaben, propylparaben, and butylparaben) were detected in 70 leave-on and 35 rinse-off samples as shown in Table II. Methylparaben was the most commonly used paraben in both categories of children's cosmetics. The detection rate of methylparaben was 93% in leave-on products and 46% in rinse-off products. The detection rates of propylparaben were 69% and 43% for the leave-on and rinse-off products, respectively. Rinse-off samples contained no butylparaben.

The frequencies of using mixed esters (more than two kinds of parabens) were higher than those of using only a single ester in cosmetics for children. The detection rates were 69% (72 of 105) and 17% (18 of 105) for the products using mixed esters and single ester, respectively. The detection rates of mixed esters were 89% (62 of 70) and 29% (10 of 35)

Table II
Frequency of Using Parabens in Cosmetics for Children

	Methylparaben		Ethylparaben		Propylparaben		Butylparaben	
Category	Number	Detection rate (%)	Number	Detection rate (%)	Number	Detection rate (%)	Number	Detection rate (%)
Leave-on products	65	93	30	43	48	69	11	16
Rinse-off products	16	46	1	3	15	43	ND	ND
Total	81	77	31	30	63	60	11	10

ND: Not detected.

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for leave-on samples and rinse-off samples, respectively. As shown in Table III, parabens were not detected in 2 of 70 leave-on samples and 13 of 35 rinse-off samples. Parabens were more often used in leave-on samples compared with the rinse-off samples as shown in Table III.

CONTENTS OF PARABENS

In general, the mean content of parabens was less than 0.10% in leave-on and rinse-off products. The maximum level of propylparaben detected in leave-on samples was 0.38%, which was close to the restriction level of 0.40% (8) as shown in Table IV. The levels of mixed esters in both categories of cosmetics were less than the restricted level of 0.8% (8). Among the 62 leave-on products with mixed esters, the levels in 2 samples were determined to be 0.75% and 0.63%, which were approaching the limitation of 0.8%. The levels in 3 samples were between 0.40% and 0.60%, 8 samples fell in the range from 0.20% to 0.39%, 27 samples were between 0.10% and 0.19%, and 22 samples were below 0.09%. Among the 10 rinse-off products with mixed esters, the levels in 2 samples were determined to be 0.20% and 0.30%, and that in the other 8 samples were below 0.10%. The level of 18 samples with monoester were all less than 0.10% in both leave-on and rinse-off samples. In addition, we found that the levels of paraben preservatives in children's cosmetics were at the same level as those in adults' cosmetics (3,4). Parabens are capable of permeating through and accumulating in the skin (9). Considering that children's body weight is less and their skin is more permeable than that of adults, the dosage of substances absorbed through skin is also higher than adults because of the high ratio between skin surface area (10). As a result, the exposure risk of parabens in cosmetics for children may be higher than those for adults. However, further supportive data are needed.

Table III
Frequencies of Using Mixed Esters and Monoester in Cosmetics for Children

Preservatives	Category	
	Leave-on products	Rinse-off products
Methylparaben, ethylparaben, propylparaben, and butylparaben	3	ND
Methylparaben, ethylparaben, and propylparaben	10	ND
Methylparaben, ethylparaben, and butylparaben	1	ND
Methylparaben, propylparaben, and butylparaben	7	ND
Methylparaben and ethylparaben	15	ND
Methylparaben and propylparaben	25	10
Ethylparaben and propylparaben	1	ND
Methylparaben	4	6
Ethylparaben	ND	1
Propylparaben	2	5
Not detected	2	13

ND: Not detected.

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Table IV
Results of the Contents of Preservatives in 105 for Children's Cosmetics

	Methylparaben			Ethylparaben			Propylparaben			Butylparaben		
Category	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum
Leave-on products	0.08	0.008	0.35	0.06	0.005	0.22	0.05	0.002	0.38	0.03	0.002	0.08
Rinse-off products	0.04	0.001	0.13	ND	ND	ND	0.03	0.001	0.11	ND	ND	ND

ND: Not detected.

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CONCLUSIONS

In this survey, contents of parabens detected in cosmetics for children in Beijing, China, were under the restricted levels. The detection rate of methylparaben in the 105 products for children was the highest, which is similar to the results of Guangdong Province and Shenzhen City. It is worth noting that the dosages of parabens found in leave-on product samples were higher than those in rinse-off product samples. Since the levels of paraben preservatives in children's cosmetics were at the same level as those in adults' cosmetics while infants and children's skin is more permeable than that of adults, further research should be performed to prove whether the level of parabens in children's cosmetics is harmful.

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