

A survey of phthalate esters in consumer cosmetic products

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Synopsis

Certain phthalate esters have been shown to cause reproductive toxicity in animal models. For this reason, the FDA has been monitoring the use of phthalate esters in cosmetics. In this study, the U.S. Food and Drug Administration (FDA) conducted a limited survey of 84 adult-use and baby-care cosmetic products for the presence of five phthalate esters: dimethyl phthalate (DMP), diethyl phthalate (DEP), benzylbutyl phthalate (BBP), dibutyl phthalate (DBP), and diethylhexyl phthalate (DEHP) (Figure 1). The analytes were extracted from a cosmetic product/Celite mixture with hexane, and the extract was then analyzed using reversed-phase high-performance chromatography (HPLC) on an instrument equipped with an ultraviolet radiation (UV) detector set at 230 nm. The analytes were separated on a Partisil octadecylsilane (ODS)-3 column (250 mm × 4.6 mm I.D., 5 μm). The mobile phase consisted of a mixture of 50% water, 34% acetonitrile, 13% 2-propanol, and 3% methanol that was changed linearly (35 minutes) to 15% water, 55% acetonitrile, 25% 2-propanol, and 5% methanol and held for an additional ten minutes. Spiked recoveries in antiperspirant and nail color ranged from 88% to 104%. Thirty-one of the 60 adult-use cosmetic products were found to contain at least one phthalate ester. Twenty products contained DEP and 11 nail products contained DBP. Concentrations of DBP ranged from 123 μg/g to 62,607 μg/g. Concentrations of DEP ranged from 80 μg/g to 36,006 μg/g. Five of the 24 baby-care products contained DEP at concentrations ranging from 10 μg/g to 274 μg/g.

INTRODUCTION

Phthalate esters are widely used by industry to impart flexibility to otherwise rigid polymers such as polyvinyl chloride (PVC), to fix or hold color or fragrance, making the color or fragrance last longer, and to provide a film or gloss, to name just a few applications (1). Because they are not bonded in their matrix, phthalate esters elute to the environment and are among the most abundant of man-made environmental pollutants (1,2). Everyday consumer products containing phthalate esters include pharmaceutical tablets and capsules, vitamins, adhesives and glues, detergents and surfactants, fishing lures, children's toys, paints and printing inks, food product containers, textiles, and household items such as shower curtains, vinyl upholsteries, and floor tiles. In cosmetic products, phthalate esters are used as skin moisturizers, as skin softeners, and as skin penetration enhancers (3,4). They are also used as anti-brittleness and anti-cracking agents in nail polishes and sealants, as anti-foaming agents in aerosols, and as solvents (3,4). Applications for specific phthalate esters depend primarily on the physical properties of the individual phthalate ester, determined by the length and branching of the dialkyl or alkyl/aryl side chains (1).

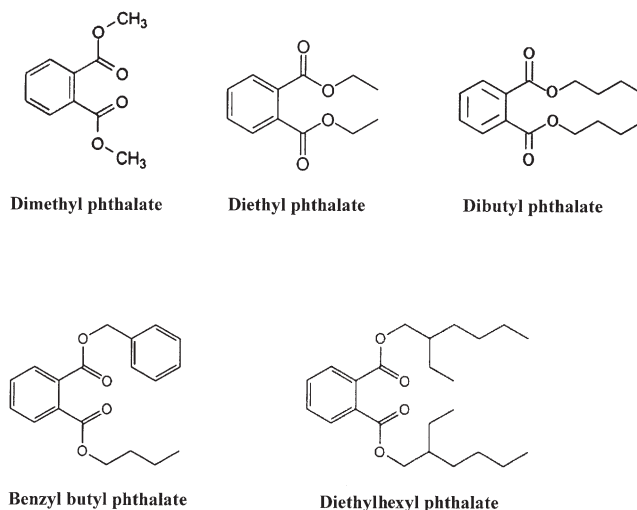


Figure 1. Phthalate esters: dimethyl phthalate (DMP), diethyl phthalate (DEP), dibutyl phthalate (DBP), benzylbutyl phthalate (BBP), and diethylhexyl phthalate (DEHP).

Exposure to phthalate esters occurs through food, the indoor and outdoor air we breathe, and our daily contact with consumer products, including cosmetics (3,5–6). In the general population, consumption of food products is generally considered to be the most significant exposure pathway (3,5,7–9). Sources include environmental uptake during crop cultivation and leaching from phthalate-containing processing equipment and packaging materials (7).

Dermal contact and absorption of phthalates via the skin is also possible. Little or no exposure occurs from products such as soaps, shampoos, and conditioners that are used frequently but then washed off the skin. Exposure can occur from cosmetics that are left on the skin for extended periods of time, with actual exposure being a function of the area of skin exposed to the product, the frequency of application and length of time left on the skin, and the absorption rate through the skin. A survey of the U.S. population has found elevated levels of the mono-esters of certain phthalates in their urine (10). Although topical exposure to phthalate esters in cosmetic products may contribute to the observed urinary levels of mono-esters (metabolites of phthalate esters) in humans, it should be noted that studies with rodents and experiments with human skin have shown that absorption through the skin of humans is most likely minimal (7). While cosmetics contribute to total exposure, no one knows what part of the total human exposure results from the use of cosmetics. Finally, medical devices containing phthalate esters may be important sources in susceptible subpopulations, including neonatal infants undergoing surgical interventions and other hospital patients receiving long-term blood, medicine, or nutritional supplements intravenously (1,5,9).

Phthalate esters have not been shown to be acutely toxic in animal models or in humans, but chronic studies in animal models, primarily the rodent, have shown developmental and reproductive toxicity (1,9,11–13). In particular, toxicological studies indicate an association between certain phthalate esters, notably dibutyl phthalate (DBP), benzylbutyl phthalate (BBP), and diethylhexyl phthalate (DEHP), and disruption of reproductive tract development in human male infants (14).

Although phthalate esters have been commercially used for over 50 years, there are only limited human data on the relationship between exposure to phthalates and human health effects (9). It is also difficult to generalize toxic effects observed in different studies with different study protocols, phthalate esters, and animal models. Nevertheless, some parties have expressed concern about phthalate esters as an entire class and have advocated for their elimination from all consumer products (15). These concerns have been further elevated by studies documenting the presence of phthalate esters and/or their metabolites in human blood and urine samples (10,13). Public interest groups, including the Environmental Working Group (EWG), continue to allege that phthalate esters used as cosmetic ingredients pose a health hazard to humans and should be banned from cosmetic products (16). The European Commission (EC), after consultation with the Scientific Committee on Cosmetics and Non-food Products (SCCNFP), also recently classified dibutyl phthalate and diethylhexyl phthalate as category 2 reproductive toxins and prohibited their use in cosmetics in the European Union (EU) (17,18).

As part of its ongoing efforts to monitor phthalate ester use, the FDA conducted a survey of consumer cosmetic products beginning in 2002 for the presence of dimethyl, diethyl, benzylbutyl, dibutyl, and diethylhexyl phthalate esters in 48 consumer cosmetic products, including hair care products, deodorants, lotions and creams, nail products, fragrances, and body washes, purchased from local stores in the Washington, D.C. area. This initial product survey of cosmetics was undertaken to verify levels of phthalate esters reported by a coalition of environmental and public health organizations, the EWG, which advocated the removal of phthalate esters from cosmetic products (19), and to collect additional data on phthalate ester levels in other cosmetic products.

The analytical method chosen for the initial and follow-up studies was originally developed in our laboratory for the analysis of phenol, resorcinol, salicylic acid, and α -hydroxy acids in cosmetic products and salon preparations (20). The analytical method utilized a Celite column for sample clean-up followed by reversed-phase HPLC separation using gradient elution, and allowed rapid and sensitive quantitation of phthalate esters in consumer cosmetic products (6). Using this method, we determined that 67% of the products surveyed contained at least one phthalate ester, while hair sprays, deodorants, nail products, and hair mousse contained two or more phthalates. The highest phthalate ester concentrations were found in nail products, with levels observed up to 60,000 $\mu\text{g/g}$. Diethyl phthalate was the most common phthalate ester found (27 out of 48 products). Dibutyl phthalate was found in ten products, while diethylhexyl phthalate was not found in any products tested. These results were consistent with those reported by the EWG in 2002 (19).

The current study is a follow-up survey to determine if any of the products analyzed in our initial survey have been reformulated to reduce or eliminate phthalate esters.

EXPERIMENTAL

COSMETIC PRODUCTS

A total of 84 adult-use and baby-care cosmetic products were purchased from local stores in the Washington, D.C. area or from the Internet. Among the 60 adult-use samples, 24 were nail enamel products, 12 were antiperspirants or deodorants, 11 were perfumes,

seven were hair products, three were lotions, two were body washes, and one was a shampoo. The products selected included products analyzed in the previous 2002 survey that had high levels of phthalates to see if any had been reformulated to reduce/remove phthalates. In addition, since nail enamels had the highest phthalate levels in the original survey, 40% of the products analyzed were nail enamels.

In response to a recent report regarding possible infant exposure to phthalate esters (21), baby-care products were included in our survey. Of the 24 baby-care products, 13 were shampoos and body washes and 11 were creams, lotions, and oils.

REAGENTS AND MATERIALS

The following reagents and materials were used: Hexane was purchased from Burdick & Jackson (Muskegon, Michigan). Acetonitrile and methanol were purchased from T. J. Baker (Phillipsburg, New Jersey). Fisher Scientific (Fairlawn, New Jersey) provided 2-propanol. All solvents were HPLC grade. Phthalate esters DMP (99%), DEP (99.5%), and BBP (98%) were purchased from Sigma Aldrich (Milwaukee, Wisconsin). DBP ($\geq 98\%$) and DEHP (99.5%) were purchased from Sigma Aldrich. De-ionized water was prepared with a Milli-Q purification system from Millipore (Billerica, Massachusetts). Celite 545 was purchased from Fisher Scientific. The extraction tubes and filter disks were obtained from Supelco (Bellefonte, Pennsylvania). Chromatographic separation was achieved using a Partisil ODS-3, 5- μm guard column (7.5 mm by 4.6 mm ID) and a Partisil ODS-3, 5- μm , analytical column (250 mm by 4.6 mm ID), both obtained from Altec Chromatography (Deerfield, Illinois).

PHTHALATE ESTER CALIBRATION STANDARDS

A primary standard solution of a mixture of the five phthalate esters (~ 1 mg/ml each) was prepared by adding approximately 100 mg of each to a 100-ml amber volumetric flask and diluting to the mark with hexane. Because of the wide range of possible concentrations in cosmetic products, three sets of working standards were prepared. One set was prepared at approximately 0.001, 0.003, 0.006, and 0.01 mg/ml by appropriate serial dilution of the stock solution. Similarly, a second set was prepared at approximately 0.01, 0.03, 0.06, and 0.1 mg/ml, and a third set for BBP, DBP, and DEHP only was prepared at 0.10, 0.30, 0.60, and 1.00 mg/ml.

SAMPLE PREPARATION

The extraction and analytical method previously developed by the FDA was used in this study (6). Briefly, approximately 1 g of each test portion was weighed into a 40-ml beaker, mixed thoroughly with about 3 g of Celite, and then transferred to a 15-ml extraction tube. The sample/Celite mixture was covered with a filter disk and was compacted firmly with a stirring rod, and then hexane was passed through the filter disk by gravity flow. The extract was collected in a 10-ml volumetric flask until the volumetric flask had been filled to the mark. For solid deodorants, the sample was first dispersed in hexane to create slurry

and then extracted as described above. To avoid sample contamination by environmental sources of phthalate esters, all glassware was thoroughly cleaned and rinsed with DI water and ethanol before use. Contact with plastics that could contain phthalate esters was avoided.

HPLC ANALYSIS

Analyses were carried out on an Agilent 1100 series HPLC. Chromatographic separation was achieved using a Partisil ODS-3, 5- μ m, analytical column (250 mm by 4.6 mm ID.) and a solvent program starting initially with 50% water, 34% acetonitrile, 13% 2-propanol, and 3% methanol that was changed linearly (35 minutes) to 15% water, 55% acetonitrile, 25% 2-propanol, and 5% methanol and was held for an additional ten minutes. The flow rate was 1.0 ml/min. The system was then gradually returned to the starting gradient and pressure for the next sample (ten minutes). Peaks were detected at 230 nm. Phthalate esters were determined in sample extracts and standards by duplicate injection of 20 μ l.

External standard calibration was used to quantitate the phthalate esters. Average peak areas were calculated for each phthalate ester, and the amount of analyte was determined using a four-point calibration curve. The limit of quantitation (LOQ), defined as ten times the baseline noise, ranged from 1 μ g/g to 10 μ g/g. Values less than the LOQ were reported as not detected. The recovery of phthalate esters from antiperspirant and nail color cosmetic products was determined by fortifying products with 100 μ g/g and 1,000 μ g/g of each ester followed by extraction and HPLC analysis as described above.

RESULTS AND DISCUSSION

The present follow-up survey was initiated to find out if any of the products analyzed previously had been reformulated to reduce or eliminate phthalate esters. To verify that the analytical method was still valid, a small recovery study was conducted. As shown in Table I, recoveries for the five phthalate esters DEM, DEP, BBP, DBP, and DEHP ranged from 88% for DBP spiked at 100 μ g/g in an antiperspirant to 104% for DBP spiked at 100 μ g/g in a nail color.

Both adult- and baby-care cosmetic products were included in the study. As shown in Table II, 31 of the 60 adult-use cosmetic products analyzed were found to contain a

Table I
Mass Recovery of Phthalate Esters from Cosmetic Products

Product	Spike (μ g/g)	Percent recovery for each phthalate ester				
		DMP	DEP	BBP	DBP	DEHP
Antiperspirant	100	94.8	97.3	98.9	88.0	97.6
	1000	98.6	96.8	97.1	94.0	100.5
Nail color	100	99.9	103.1	90.8	104.4	100.8
	1000	98.4	96.7	94.3	92.8	96.6

Average of duplicate injections of a single determination (n = 1) of each spike level.
 Mass recovery = (μ g/g_{found} \div μ g/g_{spiked}) \times 100%.

Table II
Phthalate Ester Concentrations Found in Adult-Use Cosmetic Products ($\mu\text{g/g}$)

Product type	Products tested	DMP	DEP	BBP	DBP	DEHP
Lotion	3	ND*	133	ND	ND	ND
Hair spray, gel, mousse	7	ND	80	ND	ND	ND
			153			
			181			
			316			
Deodorant	12	ND	164	ND	ND	ND
			316			
			1433			
			2699			
Fragrance	11	ND	1328	ND	ND	ND
			3036			
			5247			
			6107			
			8052			
			8669			
			10145			
			23410			
			31116			
			34479			
36006						
Body wash	2	ND	ND	ND	ND	ND
Shampoo	1	ND	ND	ND	ND	ND
Nail polish, color, enamel	24	ND	ND	ND	122	ND
					123	
					374	
					50278	
					55489	
					58765	
					59852	
					59992	
					60475	
					61065	
62607						

Average of duplicate injections of a single extraction ($n = 1$).

*Not detected ($< 10 \mu\text{g/g}$).

phthalate ester. DEP was the most common phthalate found and was present in 21 products. DBP was only found in nail products and was present in 11 of the 24 nail products analyzed. Among the 25 products comparable to those analyzed previously (6), eight no longer contained phthalate esters. Among the 13 products comparable to those previously reported by the EWG to contain phthalate esters (19), two no longer contained phthalate esters.

In terms of the distribution of phthalate esters in the different adult-use product types, four out of 12 deodorants contained phthalate ester, four out of seven hair products contained phthalate ester, 11 out of 24 nail products contained phthalate ester, all 11 fragrances contained phthalate ester, one out of three lotions contained phthalate ester, and neither of the two body washes or the one shampoo contained phthalate ester.

In the previous FDA survey results in 2002 (6), eight out of nine deodorants contained phthalate ester, 14 out of 18 hair-care products contained phthalate ester, six out of six

nail products contained phthalate ester, five out of five fragrances contained phthalate ester, three out of six lotions contained phthalate ester, two out of three body washes contained phthalate ester, and the shampoo did not contain phthalate ester.

Concentrations of DBP found in 11 of the 24 nail products ranged from 123 µg/g to 62,607 µg/g. DEP was the most common phthalate ester identified, with concentrations as high as 36,000 µg/g in fragrances.

Twenty-four baby care products were included in the current survey. As shown in Table III, five of the 24 baby-care products were found to contain DEP, which was the only phthalate ester found. Three out of 13 baby shampoos and body washes contained DEP at levels up to 274 µg/g, and two out of 11 baby creams, lotions, and oils contained DEP at levels up to 234 µg/g.

In addition to our report in 2002 (6), two other reports have described the extraction and analysis of phthalate esters in consumer cosmetic products. De Orsi *et al.* (22) have described a general procedure for the analysis of phthalate esters used in their survey of 52 commercial cosmetic products, including nail polishes, enamel removers, and nail extenders marketed within the European Union. Their method utilized ultrasonic extraction of the sample with a 90/10 ethanol/water mixture for 15 minutes at 40°C. After centrifuging the sample/extract mixture, an aliquot of the clear supernatant was collected, filtered on a Millipore filter, and injected into the HPLC instrument. Chromatographic peaks were detected and quantified at 254 nm. Due to the different polarity of the analytes, a gradient elution technique was adopted and separation was achieved with an ethanol-water mobile phase starting at 50/50 ethanol/water and changing to 95/5 ethanol/water. A photodiode array detector was used for the evaluation of peak purity factors. The phthalate esters DEP, DBP, or DEHP were found in 16 of the 52 cosmetic products at concentrations between 0.3% and 3.0%. As noted by the authors, the cosmetic products, purchased prior to January 1, 2005 and found to contain DBP or DEHP, will have to be reformulated by their respective manufacturers to comply with the EU prohibition on the use of DBP and DEHP.

Shen *et al.* (23) described a method for the determination of phthalate esters in cosmetic products, including hair sprays, perfumes, deodorants, creams, and lotions. Phthalate esters were extracted using sonication in methanol, cleaned up with an octa carbon chain bonded silica stationary phase (C8) solid-phase extraction (SPE) column, and then separated on a C8 HPLC column with gradient elution with a methanol/water solution. Phthalate esters were detected with a diode array detector at a wavelength of 230 nm. In an analysis of

Table III
Phthalate Ester Concentrations Found in Baby-Care Products (µg/g)

Product type	Products tested	DMP	DEP	BBP	DBP	DEHP
Baby shampoo and body wash	13	ND*	10 55 274	ND	ND	ND
Baby cream, lotion, and oil	11	ND	114 234	ND	ND	ND

Average of duplicate injections of a single extraction (n = 1).

*Not detected (< 10 µg/g).

15 cosmetic products, only one was found to be free of phthalate esters. In the remaining 14 products, the phthalate esters DEP, DBP, DCHP (dicyclohexyl phthalate), and/or DEHP were found with concentrations ranging from 0.00012% to 0.53%.

CONCLUSION

In this report, a follow-up survey of 84 cosmetic adult-use and baby-care products for the presence of five phthalate esters, DEM, DEP, BBP, DBP, and DEHP, is described. Only DEP and DBP were found in adult products, and DBP was only found in nail products. Concentrations of DBP ranged from none detected to 62,607 $\mu\text{g/g}$. Concentrations of DEP ranged from none detected to 36,006 $\mu\text{g/g}$, with DEP being the most commonly found phthalate ester. For adult-use cosmetic products, concentrations of DEP above 10 $\mu\text{g/g}$ were found in fragrances, and concentrations of DBP above 10 $\mu\text{g/g}$ were found in nail products. In baby-care products, DEP was the only phthalate ester found. Concentrations of DEP ranged from not detected to 274 $\mu\text{g/g}$. DMP, BBP, and DEHP were not detected in any products.

The results of this follow-up survey suggest that there is an effort to reformulate cosmetics products to reduce the use of phthalate esters in cosmetic products. Eight of the 25 products that were analyzed in our previous survey (6) no longer contained phthalate esters. Two of the 13 products that were comparable to those reported by the EWG in 2002 to contain phthalate esters (19) no longer contained phthalate esters. A comparison of the results obtained in the initial product survey (6) and this follow-up survey also suggests that there have been changes in the use of phthalate esters in some types of cosmetic products. The 2002 product survey (6) found phthalate esters in five out of six of the nail products, while in this follow-up survey phthalate esters were found in 11 out of 24 nail products. No change in the use of phthalate esters was noted for fragrances.

The FDA will continue to monitor adult- and baby-care cosmetic products for the presence of phthalate esters as well as for any new materials that may have replaced them. The FDA does not have evidence at this time that the levels of phthalate esters present in cosmetic products are harmful to consumers as these products are currently used. If the FDA determines that a health hazard exists, the agency will advise the public and the industry, and it will take appropriate action to protect public health.

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