Generic vs. Name Brand

Where is your money going?

INTRODUCTION

Consumers are attracted to the low cost of generic over name brand cosmetics. These generic brand products are marketed to be comparable to their respective name brand equivalents. This research group examined this claim using three pairs of cosmetic products as the testing pool. The name brand products are Olay® lotion with ultraviolet (UV) protection, Aveeno® Active Naturals® body wash, and Pantene® Pro-V shampoo with conditioner. All generic equivalents are sold under the Equate® brand and are available exclusively at Wal-Mart locations. To complete the project goal, three fingerprinting techniques were used to compare product composition, two physical properties of the products were determined, and an active ingredient in the lotion was quantified. In addition, a panel evaluated product performance.

BACKGROUND

Liquid Chromatography with Mass Spectrometry detection (LC-MS) was used to fingerprint all the products. In liquid chromatography, samples are carried through a column by a liquid mobile phase. A mixture of water and acetonitrile was used as the LC mobile phase. Based on their structure, compounds vary in their interactions with a solid-phase column. The differences in attraction separate the compounds and cause them to exit the column at different times (elute).[1] After eluting off the column, product samples were pushed through a needle held at a high electric potential to convert neutral molecules to charged droplets. This technique, Electrospray Ionization (ESI), produces gaseous ions, which are necessary for detection by mass spectrometry, by evaporating the solvent under low pressures and high temperatures.[2,3] The gaseous ions were separated according to their masses and charged and detected by a mass spectrometer. Total Ion

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Chromatograms (TIC) and mass spectra were produced to compare the pairs.

Proton (^{1}H) Nuclear Magnetic Resonance (NMR) Spectroscopy is an analytical method utilized to characterize compounds based on the chemical shifts of each compound present in the sample. Every multiplet in the NMR spectra corresponds to a proton in a different chemical environment. Identical proton shifts will indicate that the products contain structurally similar or identical compounds. Because each of the products is water-based, a proton NMR spectrum on straight sample would show a very large water peak providing relatively unimportant information and obscuring potentially useful information. Therefore, for each of the six products an aliquot of approximate mass 1.0g was placed into a desiccator to dehydrate the samples. After two weeks the aliquots were sufficiently dehydrated and prepared by adding approximately 3mL of D_2O to each of the six samples. ^{1}H NMR spectra were taken using a 500MHz instrument. To compare spectra, the spectra were aligned in a manner conducive to elucidating differences between the spectral proton shifts.[4]

The two lotions each contain two active ingredients: octinoxate and zinc oxide. These ingredients are responsible for the SPF 15 UVB protection of the lotions by absorbing the light and emitting it as less harmful light.[5] Both products list the zinc oxide concentration as 3.0%. The FDA has determined that zinc oxide is safe at levels below 25%.[6] Flame Absorption Atomic Spectroscopy (FAAS) was used with standard additions to quantify the zinc oxide in the samples to both compare the two products and test the advertised concentration based on methods of Salvador et al.[7] The method of standard additions involves adding known amounts of a standard to the sample, which allows the concentration of zinc oxide in the sample to be determined by extrapolation of the calibration curve. Octinoxate has been approved by the FDA at levels below 7.5%.[8] It is listed in both products at 6.0%. Salvador, et al.[9] were able to quantify octinoxate in sunscreens using HPLC with UV spectrophotometric detection and standard additions.

Since these products are used on the body, physical properties may play an important role in the overall feel and performance of the products. The density of any substance is determined by dividing mass by volume. The pH value of a solution is defined as the negative logarithm of hydronium ion concentration in the solution. Based on the value of the pH, a solution is categorized as acidic, basic, or neutral.

A fingerprint of each product was obtained using a High-Performance Liquid Chromatography (HPLC) system with Ultraviolet detection on a C_{18} column. A 100 mL dilution of all samples was prepared by diluting approximately 2g of the product with methanol. 20μL of this was then injected into the system. For the body washes and shampoos, a mixture of water and acetonitrile (ACN) was used for the mobile phase based on the work of Kiyoshima et al.[10] The mobile phase composition was held constant for the body washes (isocratic elution), but for the shampoos, the organic concentration was increased in order to elute the more retained compounds (gradient elution). The lotions were separated using an HPLC system with a diode array detector, taken from the work of Salvador, et al.[11] and a mobile phase of water and methanol.

RESULTS

The TICs of the Pantene® and Equate® shampoos showed multiple peaks with matching retention times, suggesting that many compounds were found in both shampoos

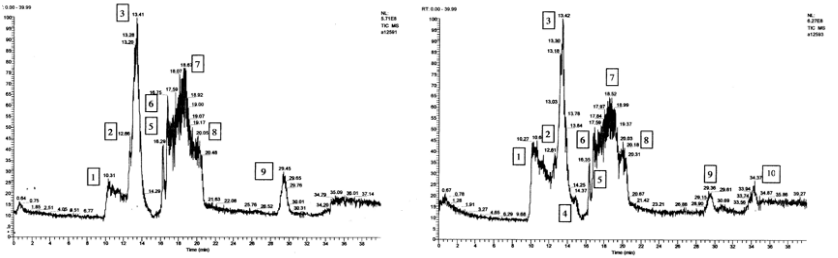

Figure 1. Total Ion Chromatograms of Pantene® (left) and Equate®(right) Shampoo

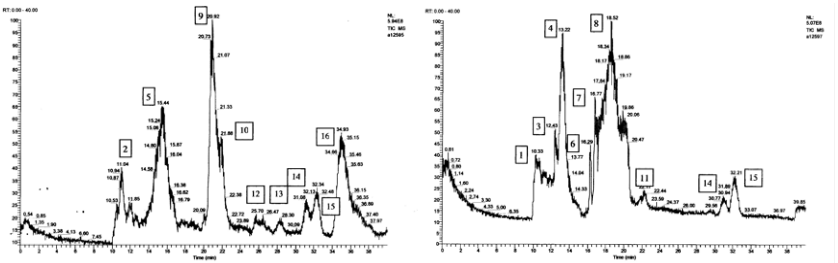

Figure 2. Total Ion Chromatograms of Aveeno®(left) and Equate®(right) Body Wash

(Fig. 1). Peaks 3, 5, 7, and 9, with approximate retention times of 13.4 minutes, 16.3 minutes, 18.5 minutes, and 29.4 minutes, respectively, are notable examples of peaks found on both TICs. The TIC of the Equate® shampoo had a few extra peaks (4 and 10) that are absent from the TIC of the Pantene® shampoo, indicating the presence of several unique ingredients. Nearly identical mass-to-charge peaks in the average mass spectra of both shampoos support the similarities of the TICs. Evenly spaced peaks separated by a mass-to-charge ratio (m/z) of 44 suggest that a polymer was present with chain unit masses of 44 atomic mass units (amu). The Pantene® shampoo contains a polyethylene glycol, a family of polymers with repeating CH_2-O-CH_2 units, that have a mass of 44amu. Polymers are identified by the number of units in their chains or their masses, but their names and formulas represent average masses. Because some variation exists in the chain length, the products contain polymers with an array of different masses. The set of peaks 44m/z apart in the Pantene® mass spectra appears to represent a series of polyethylene glycols with different numbers of units.

A few of the peaks on the TICs of the body washes had matching retention times (Fig. 2). Peaks 14 and 15, with retention times of approximately 31.0 minutes and 32.2 minutes, respectively, were present in the TICs of both body washes. An additional peak in the TIC of the Equate® body wash, peak 11, eluted at about 22.2 minutes. There is no distinct peak matching in the Aveeno® body wash TIC, but a larger peak may be hiding the corresponding peak. The remaining peaks were unique to either the Aveeno® or Equate® body wash. The indication of formula

difference is further supported by the mass spectra. The mass spectrum of the Equate® body wash also suggests the presence of a polymer with peak separations of 44 m/z. Some peaks in the mass spectrum of the Aveeno® body wash are 44 m/z apart, but in general, separations between adjacent peaks are less uniform. The spacing differences may reflect the detection of additional compounds in the Aveeno® body wash formulation. Both products contain polyethylene glycol, which may have produced the series of peaks.

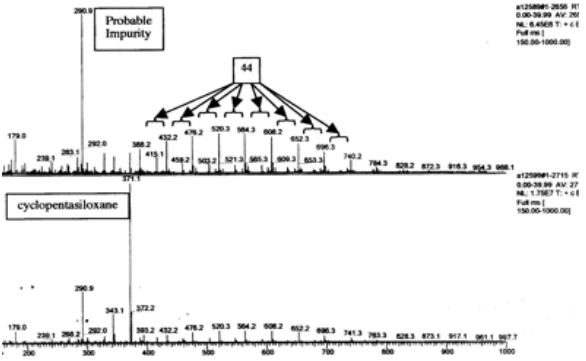

Figure 3. Mass Spectra of Equate® Lotion (Top) and Olay® Lotion (Bottom)

The lotion TICs had fewer distinct peaks than either of the other two pairs of products. Three peaks, with retention times of approximately 12.5 minutes, 13.3 minutes, and 18.5 minutes, were among the major similarities between the TICs of the Olay® lotion and the Equate® lotion. There was at least one distinct peak present in the TIC of the Equate® lotion that was missing from the TIC of the Olay® lotion, suggesting that the Equate® lotion may have additional ingredients. The averaged mass spectra of both lotions also indicated the presence of a polymer with units of 44 m/z (Fig. 3). The polymer may be a polyethylene glycol, which is present in both lotions. The mass spectrum of the Olay® lotion has a strong peak at 371.1 m/z, and a smaller peak appears at a similar mass-to-charge ratio in the Equate® lotion mass spectrum. This peak probably corresponds to cyclopentasiloxane, which has a monoisotopic mass of 371.1amu and is an ingredient in both lotions.

A peak at 290.9 m/z was present on all averaged mass spectra. The molecular mass of octinoxate is

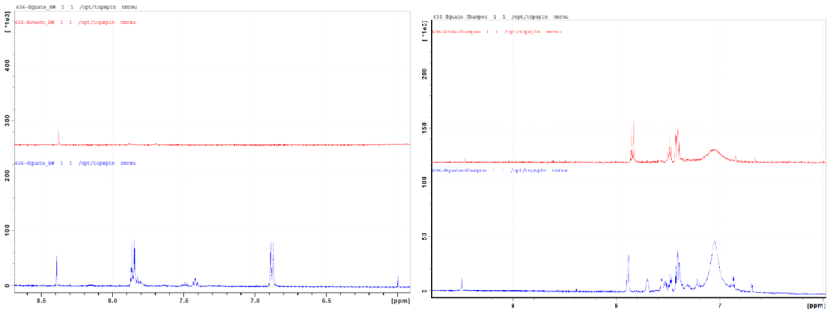

Figure 4. NMR Fingerprints of Aveeno® Top) and Equate® Body Wash (Bottom) on left and Pantene® (Top) and Equate® Shampoo (Bottom) on right

290.2amu, but a universal impurity is the more likely cause of the peak. All mass spectra also show peaks at 179.0 m/z, indicating the possible presence of another impurity.

For qualitative comparisons of product formulations, the retention times of major peaks are the only reliable data that can be gained from the TICs. The samples were not originally prepared in identical concentrations and additions of differing amounts of methanol for subsequent sample reconstitutions further alter concentrations. Because the concentrations of the samples vary, comparisons of peak width, shape, and area, information often used for quantification are not valid. Compared to chromatograms produced by other separation techniques, TICs usually have relatively broad peaks, which is desirable because mass spectrometry takes time to detect a sample. If a compound elutes during a very brief time period, there is less time to analyze the eluent sample. However, broad peaks increase the probability of interference as one peak may contain the elution of multiple compounds which complicates analysis and quantification. Finally, electrospray is not a universal ionizer. Some of the ingredients may not have been ionized and therefore would not be detected by the mass spectrometer.

Qualitative analysis was performed on each of the samples' NMR spectra. The body wash samples appear quite different upon analysis. Though the region from 1.0 to 6.0 parts per million (ppm) appears to be similar, the region of interest for these compounds is the aromatic region. In the aromatic region of the spectrum from 6.0 to 8.0ppm, the Equate® body wash has multiplets 1 and 2 which the Aveeno® product lacks (Fig. 4). This suggests a difference in formulation between the two products. The Equate® product contains a structurally different aromatic compound than the Aveeno® product. The two lotion samples' spectra show no proton shift differences in the region from 0 to 4.4ppm. In addition, the aromatic region of the shampoo spectra shows identical proton shifts. The high correlation between the two spectra supports high similarity in formulation between the two products. The NMR spectra of the two shampoo samples show almost identical shifts in all regions of the spectrum. The only difference comes in the aromatic region. Peak 1 has a slightly different shift in either of the products (Fig. 4). In addition, peak 2 is present in the Equate®, but not the Pantene® shampoo. The main difference between all the sets of spectra is the peak intensities between samples, which is most likely due to differences of concentration between the two prepared samples, since identical masses were not weighed for each.

Comparing the two chromatograms of the HPLC-UV-Vis for the Aveeno® and Equate® body washes (Fig. 5), there are several corresponding peaks present in both chromatograms. Peaks 1,2, and 3 eluted at 1.5,2, and 5.2 minutes. Peaks 4, 5, and 6 appeared at 9.5, 15 and 17.5 minutes in the Aveeno® body wash, but not in the Equate® body wash. The two body wash chromatograms indicate that the Aveeno® and the Equate® body washes have some similar components, but do not have identical formulations. The chromatograms of the Olay® and Equate® lotions (Fig. 6) both showed peaks 7, 8, 9, and 10 with retention times of 3, 4, 7, and 15 minutes, respectively. This indicates that the two products are relatively similar, but based on the respective intensities between peaks in a single product; the ratio of compounds differs between the products. The chromatograms of

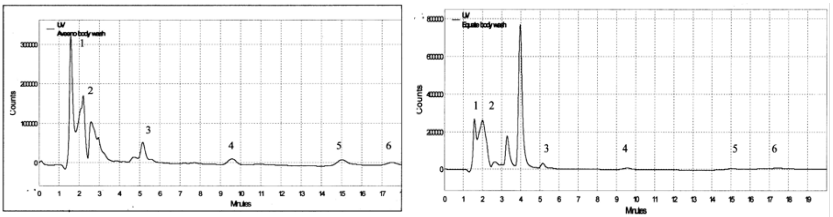

Figure 5. HPLC Chromatogram of Aveeno® Body Wash(left) and Equate® Body Wash(right)

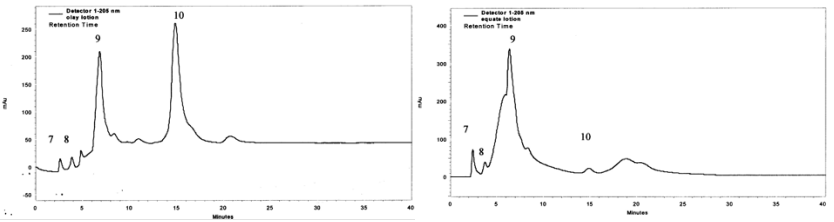

Figure 6. HPLC Chromatogram of Olay® Lotion(left) and Equate® Lotion(right)

the Pantene® and Equate® shampoos had several peaks similar to one another (Fig. 7). Peaks 11-19 appeared in both chromatograms at similar retention times. Of the three products, the shampoos' chromatograms showed the most similarities.

To quantify the zinc oxide, first, the instrument response was found to be linear in the 0.1ppm to 1.0ppm range. The limit of detection was calculated as 0.117ppm, while the limit of quantization was 0.389ppm. Through method development, it was found that the addition of hydrochloric acid to the sample increased the measured amount of zinc because the acid dissolved more zinc into the solution to be detected. The method was also improved by using a known certified zinc standard rather than dissolving solid zinc with hydrochloric acid. By testing various methods, it was found that obtaining an exact value for the concentration of zinc oxide was difficult because of the large dependence on the method of sample preparation. However, all 5 methods used showed the Equate® lotion had a statistically significant higher concentration of zinc oxide, with over 98% confidence. Each method involved performing standard additions. The calibration curve from the Equate® lotion using the optimal method, number 5, showed a correlation of 0.9813 and 0.9292 for Olay®. While these are not exceptionally high, they were sufficient to show a difference between the two products, even with the error. All calibration curves from the other methods showed high correlation above 0.99. On these graphs, the concentration of zinc in the sample corresponds with where the line crosses the x-axis. The results from all the methods were compiled (Tab. 1).

One original goal of this research was to quantify the other active ingredient in the lotions, octinoxate. However, several factors made it unrealistic to accurately achieve quantification. The commercial standard obtained was only 98% pure. The chromatogram of the commercial standard showed several peaks, indicating multiple components.

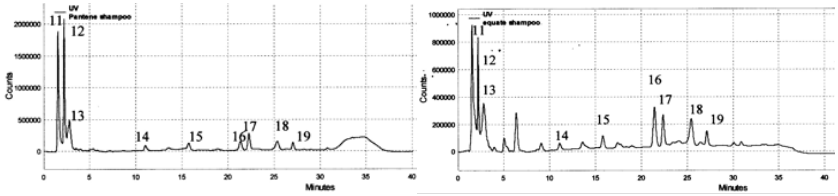

Figure 7. HPLC Chromatogram of Pantene® Shampoo(left) and Equate® Shampoo (right)

Several trials produced different chromatograms, making it difficult to identify the peak for octinoxate. Without a pure standard, the added concentration for standard additions would be unknown and quantification would be impossible.

The densities of the products were essentially the same except for those of the body washes. The body washes also showed the greatest difference in pH between the name brand and generic. The pH values of the name brand and generic shampoos and lotions were very similar, but the pH values of the two body washes differed by a value of 1.94, meaning that the Equate® body wash is almost one hundred times more acidic than the Aveeno® body wash.

Product testing suggests that the name brand was preferred over the Equate® for all three products by a 3:2 ratio in the body washes, a 4:1 ratio in the shampoos, and a 3:2 ratio in the lotions. The Aveeno® body wash has an overall better smell and was smoother, though the Equate® body wash foamed well. The Pantene® shampoo seemed to keep the hair less dry, while the Equate® lathered the hair well but left the hair frizzy. The Olay® lotion and the Equate® lotion had different characteristics but the Olay® lotion was preferred. The Olay® brand moisturized the skin better and kept the skin drier for a longer period of time; the Equate® coated well but left an oily texture.

CONCLUSION

In conclusion, the majority of our results indicate that while there are similarities between generic and name brand products, they are not as similar as consumers may be led to believe. Most of the fingerprinting

Table 1. Zinc Oxide Concentrations from Various Methods

	Method 1	Method 2	Method 3	Method 4	Method 5
% Zinc in Olay®	2.2% ± 0.5%	2.83% ± 0.02%	1.87% ± 0.04%	2.95% ± 0.02%	2.182% ± 0.010%
% Zinc in Equate®	2.7% ± 1.2%	3.16% ± 0.02%	2.44% ± 0.10%	3.69 ± 0.01%	3.367% ± 0.004%
%Confident different	98.1%	100%	100%	100%	100%

methods indicated that the name brand and generic products have some differences in their chemical formulations. The body washes showed the most differences in many of the fingerprinting tests, while the shampoos showed the greatest difference in consumer preference testing. The concentrations of ingredients may vary, but their affects on product performance are not always clear. Some compounds are vital to a desired function. Other ingredients are present as fillers or serve relatively trivial purposes and could easily be substituted without major changes in consumer satisfaction. The best product for a particular consumer may depend on personal preference and budget. The percentage price difference between name brand and generic products was greatest for the shampoos and least for the body washes (Tab. 2). However, the criticisms of the Equate® products did not relate to the amount of product needed but to the quality of product, so a simple cost analysis is not necessarily adequate to determine the best value. If cost is a priority, generic products will likely be favored; they serve the basic functions of the products. Some consumers may find the slightly higher prices of name brand cosmetics are justified by improved product performance. Although a general consensus was achieved for two of the pairs, the sample size was small. Future product testing would benefit from blind performance trials among a large, diverse testing pool. Further research could seek to determine which chemicals were present in different amounts and how formula differences affect product performance. In addition the techniques outlined in this paper may be applied as analytical techniques for elucidating formulation differences between products. The analytical methods could be used to compare the known name brand products with the supposed counterfeits in foreign countries where counterfeit products rampant.[12]

Table 2: Walmart Prices of Products in Lawrence, KS

Product	Size	Price*	Percent Price Difference
Pantene® Shampoo	25.4 liquid ounces	$5.47	75.3%
Equate® Shampoo	25.4 liquid ounces	$3.12	
Olay® Lotion	6 liquid ounces	$9.47	68.5%
Equate® Lotion	6 liquid ounces	$5.62	
Aveeno® Body Wash	12 liquid ounces	$5.97	53.9%
Equate® Body Wash	12 liquid ounces	$3.88	

END NOTES

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