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The Absorption and Desorption of Cosmetic Chemicals on Skin

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Synopsis—Stratum corneum in the form of excised CALLUS was used to measure the effect of various aqueous solutions on SKIN. Pieces of callus were immersed in distilled WATER, in ORGANIC SOLVENTS, and in aqueous solutions of DETERGENTS, HUMECTANTS, and SOAPS for different lengths of time. The weight increases were compared with the increases obtained by water alone. Repetitive soaking of callus in the same solution, alternating with air-drying, was investigated. The results allow a discussion of the factors which influence the water content of skin and the conservation of this water.

INTRODUCTION

It is well known that skin from various locations on the human body has different properties. Also, skin from different individuals behaves quite distinctly (1). Striking data to this effect can be found in a publication by Marzulli (2), who measured the resistance of penetration by different areas of human skin. He found that steady-state penetration rates were remarkably consistent for each tissue specimen. However, biological variations were quite considerable; thus, for the same location on the body, the penetration rates would vary by as much as a factor of 100.

In previous publications, we have reported on the effect of presoaking with various surfactant solutions on the skin-water contact angle (3, 4). It was found that various cationic surfactants and amine oxides lowered the skin-water contact angle at the lowest concentration. Rinsability data supported findings and suggested that cationic surfactants are tightly bound to the skin.

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The present paper adds to our general knowledge of the properties of human skin with regard to permeability, substantivity, and softening under experimentally controlled circumstances. The methodology is described and results obtained with distilled water, organic solvents, detergents, soaps, and humectants are discussed.

Characteristics of Callus

Calluses occur on the soles or edges of the feet where there is excessive friction. An acute excess will produce a blister, while chronic friction produces a callus. Clinical inspection shows no special structural changes, only hyperkeratosis (5). The cellular stratification of the epidermis is simply a reflection of the various stages through which basal cells of the stratum germinativum pass in their gradual conversion into the horny material of the stratum corneum (6).

Callus samples from different human donors behave very differently from one sample to another. This fact has influenced the methodology of our investigation to the extent that each experiment was performed jointly on one half of a callus piece with the other half as a control experiment.

Methodology

Calluses of approximately equal size (about 7 mm^2) were cut in half. One half was weighed and immersed in distilled water, the other half was weighed and immersed in the experimental solution. In all subsequent operations, such as removal from solution and weighing, both the control and the experimental sample were handled the same way and in close succession. This procedure greatly reduced the experimental error due to differences in exposure lengths and to fluctuations in ambient relative moisture content.

The method was adopted because we were interested in measurable changes in the region of low relative humidity. Results by Blank (7) and Singer and Vinson (8) indicate that there is little fluctuation in moisture uptake of stratum corneum in the region of around 20% RH when the relative humidity changes a few per cent; our measurements were thus taken at 20% RH and 22°C.

Experimental and Results

Uptake and Release of Water by Callus Immersed in Distilled Water

Calluses were immersed in distilled water for different lengths of time. The water uptake was determined within 5 min after the sample

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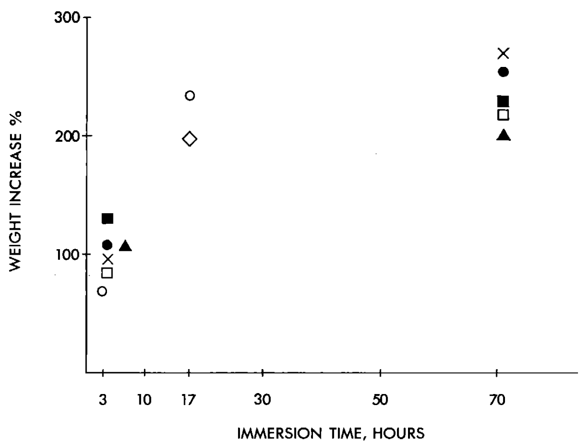

Figure 1. Uptake of water by callus immersed in distilled water showing weight increases as function of immersion time. Different symbols are used to represent individual samples

was removed from the water. These experiments illustrate the difference in properties which exist from one callus piece to another (Fig. 1).

As expected, the water uptake is increased as a function of immersion time. The individual differences between callus samples stress the importance of controls on an identical piece of callus.

Callus samples swollen by immersion in water were dehydrated by exposure to the environmental conditions of the laboratory (Fig. 2).

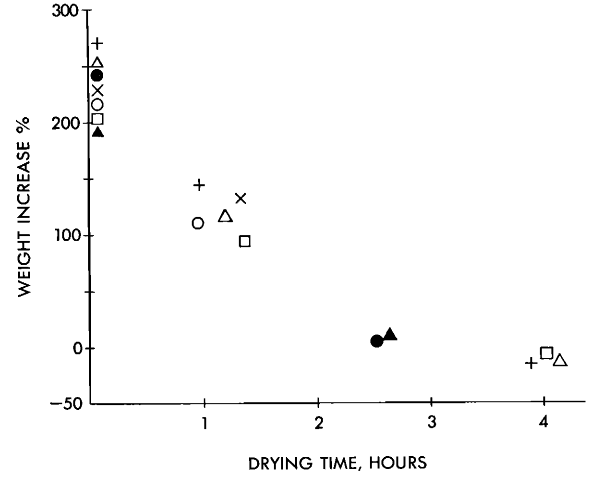

Figure 2. Loss of water from callus swollen by 24 hours immersion in distilled water. Weight increases or decreases as compared to the original callus dry weight as function of drying time

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Rapid initial dehydration was followed by much smaller changes until equilibrium was reached. The dehydration is a function of the relative humidity of the laboratory atmosphere and of air circulation. The rate of dehydration was quite uniform for the individual callus pieces. There was no overlapping of the sorption and desorption curves, an effect well known as hysteresis.

Organic Solvents

The action of organic solvents on callus has been reported previously (7, 9). We repeated some of the earlier work; besides the fact that such experiments are valuable in providing figures for lipids and other extractibles, we wanted to compare results of earlier workers with our own.

Blank (7) and Middleton (9) reported that the composition and amount of human epidermal lipids is significant for the retention of water by the stratum corneum and, hence, the softness of the skin. The composition of skin surface lipids shows considerable variations both in different areas of the body of the same individual and in the same area of the body of different individuals (10). The lipid content of the epidermis of the human sole was found to be consistently lower than the lipid content of the epidermis from other regions (11). The lipid composition of the epidermis also changes during the process of keratinization (12). The phospholipid and cholesterol contents of the cells of the epidermis decrease greatly during keratinization. It can thus be expected in our experiments with surfactants and humectants that the water-binding capacity of callus will reflect more the properties of keratinous materials than the properties of skin lipids.

Blank (7), and later Middleton (9), found that extraction of callus with an organic solvent, followed by water, extracted much more substance from the callus than extraction by either water alone or water followed by organic solvent. We were not successful in duplicating

Table I
Solvent Extraction of Callus Pieces

Extraction Sequence	Weight Loss[a] (%)
Water-acetone-water-acetone	10.7
Water-alcohol-water-alcohol	17.0
Water-pyridine-water-acetone	12.5
Water-alcohol-chloroform-alcohol	15.4

[a] Of experimental in excess of weight loss of water-extracted control.

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Blank's results; however, we extracted up to 17% material from callus with various organic solvents when the callus was previously swollen in water. Table I indicates the solvent systems used and the weight losses obtained. These experiments indicate that other materials besides lipids are extracted from callus with organic solvents and the assistance of water.

Extraction of Water-Soluble Substances from Callus by Surfactants

The following surfactants were examined: sodium lauryl sulfate, sodium lauroyl isethionate, polyoxyethylene sorbitan monostearate (Tween 80),* cocoyl sarcosine, and sulfated ethoxylated fatty alcohol.

Sodium lauryl sulfate and sodium lauroyl isethionate were chosen to allow direct comparison with the results obtained by Middleton (13) who worked with guinea pigs' footpads. He found a somewhat greater extraction of water-soluble substances by the use of sodium lauryl sulfate than by the use of sodium lauroyl isethionate: 9.5% *versus* 7.9%. We found increased extraction by isethionate; this was more pronounced at higher concentrations (Fig. 3). The immersion time for the various callus pieces was 24 hours, and the drying time was 3 days.

Thus, different surfactants had different solubilizing capacities, and these became more evident at higher concentrations. At the lower surfactant concentrations, there may have been an overlapping between

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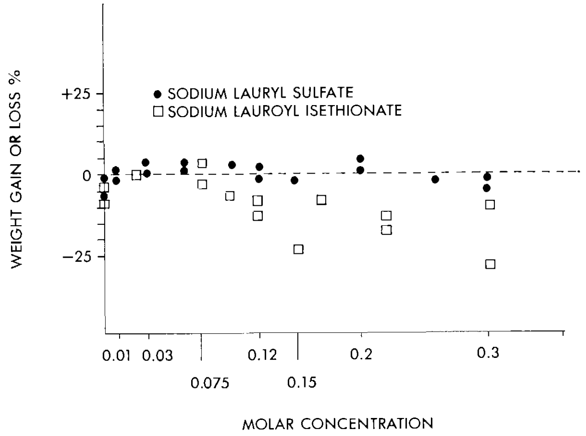

Figure 3. Weight gain or loss after drying of experimental moieties of callus immersed 24 hours in surfactant solutions of different concentrations as compared to the weight loss of the control callus moiety immersed in water

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Table II

Water Retention of Callus Halves Immersed in Tween 80, or Water, and Dried

Drying Time	Weight Change,[a] (%) 5 min	80 min	1 day	5 days
	1st Immersion (22 hours)			
30% surfactant	230.0	58.4		2.3
Water	212.2	37.9		−8.6
50% surfactant	114.2	42.8		−4.5
Water	155.0	46.0		−4.5
	2nd Immersion (48 hours)			
30% surfactant	326.0		6.4	
Water	302.0		−16.3	
50% surfactant	128.0		−2.6	
Water	209.0		−6.1	

[a] Minus sign indicates weight loss.

surfactant absorbed in stratum corneum and extraction of water solubles from callus. At the higher concentrations, it appeared that some surfactants had greater solubilizing capacity than others.

Table II summarizes results obtained with Tween 80. With a 30% Tween solution, callus absorbed more water than callus immersed in water. With a 50% Tween solution, the opposite took place. Callus immersed in 30% Tween solution retained more material all the way through the drying cycle. With the 50% Tween solution, there was less water retained by callus through the drying cycle than with water. It does not seem from the weights after 1 and 5 days' drying time, that Tween was absorbed by callus. Thus, differences in ultimate weight gain or loss and differences in water-retention capacity were observed according to the concentration of this surfactant.

This finding is interesting, since the same compound can be used in a concentrated form as an ointment, or diluted as a component in a cleansing formulation. Table II shows a duplication of effect when the operation was repeated although the length of immersion the second time was 48 hours instead of 22 hours.

Cocoyl sarcosine dispersions ranging from 1 to 20% concentrations were chosen as representative of an acidic surfactant system. The pH of these dispersions ranged from 3.1 to 3.8. Results are summarized in Table III. As can be noted, a high amount of weight gain represents a high amount of cocoyl sarcosine absorbed by the stratum corneum. As the concentration was increased to 20%, the callus weight after drying

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Table III
Water Retention of Callus Halves Immersed in Cocoyl Sarcosine,[a] or Water, and Air-Dried

Drying Time	Weight Change[b] (%)		
	15 min	1 hour	24 hours
1% surfactant	194.5	159.5	7.3
Water	213.0	98.3	−27.1
3% surfactant	153.0	133.5	17.1
Water	108.2	93.8	−7.4
10% surfactant	133.0	95.0	35.7
Water	163.0	79.8	−23.7
20% surfactant	161.5	124.5	33.5
Water	197.0	163.5	−8.8

[a] 1 to 20% aqueous dispersions.
[b] Minus sign indicates weight loss.

Table IV
Water Retention of Callus Moieties Immersed in $RO(CH_2CH_2O)_xSO_3Na$, or Water, and Dried

Drying Time	Weight Change[a] (%)	
	1 hour	24 hours
0.6% surfactant	42.9	1.4
Water	15.3	1.3
1.8% surfactant	10.0	−0.7
Water	7.6	2.8
6.0% surfactant	47.3	2.9
Water	32.3	1.9
12.0% surfactant	12.4	1.7
Water	3.1	2.1

[a] Minus sign indicates weight loss.

also increased. Moreover, while the experimental half generally picked up less water than the control, as shown in the 15-min drying time column, it retained the water generally longer than the control.

The results obtained with a sulfated ethoxylated long-chain alcohol are shown in Table IV. The concentrations tested ranged from 0.6 to 12%. It was found that, with these solutions, the water-absorption capacity of the callus increased without the surfactant apparently being absorbed in the callus.

These experiments with a few randomly selected surfactant solutions indicated that such solutions are able to modify water-retention capacity

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of stratum corneum; that some solutions extract more solubles from skin than others; and that there are variations in the amounts of surfactant absorbed onto skin.

Experiments with Soap

The rate and amount of swelling of calluses was examined as a function of concentration of toilet soap (Table V). The weight increases of callus halves at different immersion times were measured. The results indicated that throughout the concentration range of 0 to 2.4% soap solution, the callus immersed in soap solution absorbed more water than callus immersed in distilled water. These differences increased as either the soap concentration or the immersion time increased. The swelling did not increase linearly with the soap concentration or with the length of immersion.

Table V
Swelling of Callus Immersed in Soap Solutions of Various Concentrations and in Water

Soap concentrations, %	Per Cent Swelling						
	0.6		1.2		1.7	2.4	
Immersion time, hours	4.5	70	4	70	21	1.5	23
Soap solution	137.0	245.0	135.0	267.0	257.5	116.0	208.0
Water control	132.0	229.0	111.0	203.0	208.5	82.2	177.0
Difference	5.0	16.0	24.0	64.0	49.0	33.8	31.0

The weight increase of callus after immersion in aqueous solutions of a number of toilet soaps was examined. Bar A was a standard 85/15 tallow coco soap without additives; Bars B to E represented commercial soaps with various "cosmetic"-type additives, such as mineral oil or cocoa butter; Bars F, G, and H were deodorant soaps, while I and K were soap-synthetic combinations.

Results obtained are shown in Fig. 4. It was found that in almost every instance soap enhanced the water uptake by stratum corneum. Pure soap base, A, in Fig. 4, had the highest swelling power of all the soaps we examined. Concurrent with water uptake during the immersion cycle, dehydration of hydrated callus was monitored (Table VI). The negative values may be due either to material leached out from the callus piece, or to superficial cells which desquamated.

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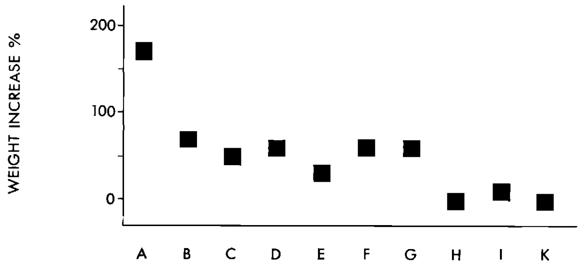

Figure 4. Behavior of callus pieces immersed 21 hours in solutions of various soaps A to K. Difference between the weight increase of a callus moiety immersed in soap solution and the weight increase of the control moiety immersed in water

Table VI
Influence of Drying Time on Weight Loss

	Differences (%) from Original Weight[a]					
Drying Time, Hours	1	3	4.5	5.5	48	120
1.7% soap E			−4.6			−12.2
Water			3.3			−7.2
2.5% soap E		15.8		11.6	3.8	
Water		14.7		6.7	0.8	
2.4% soap H	78.3					−8.8
Water	23.9					−10.4

[a] Minus sign indicates weight loss.

The graphic representation (Fig. 5) shows the per cent difference between a callus half swollen in soap solution and one swollen in water during the drying cycle. Immediately after immersion, the lines in Fig. 5 are long, indicating a great difference in weight increases. As drying time progresses, the lines become shorter, indicating that soap and water-soaked callus halves tend to reach the same weight gain or weight loss as compared to their original weight. The spread in weight loss after drying 5 days between the callus piece tested in soap solution and the control callus piece immersed in water becomes very small.

Figure 6 shows the difference between one moiety of callus piece immersed in soap solution and the corresponding moiety immersed in water. The values were recorded after a drying time of 5 days. All soaps did not behave identically: Soaps C, D, E, F, and I reverted after drying for 5 days to a slightly lower weight in the experimental callus half when compared to the control half. These values indicate that slightly more water-solubles were extracted from the callus pieces immersed in

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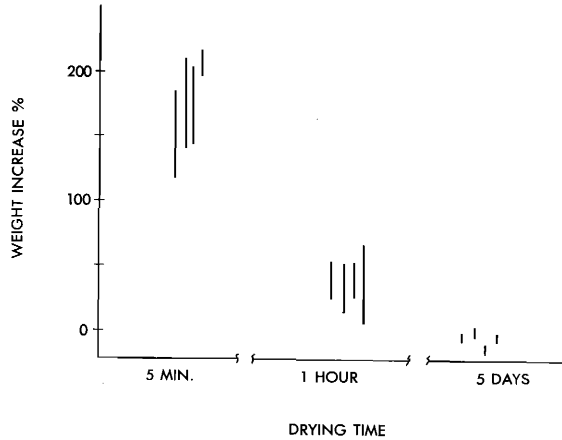

Figure 5. Drying cycle of callus pieces immersed 21 hours in soap solutions. Upper end of one of the vertical lines indicates the weight increase of the experimental half immersed in a particular soap solution, while the lower end indicates the weight increase of the corresponding control half immersed in water

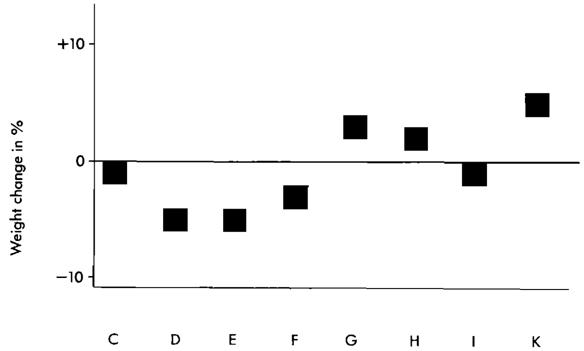

Figure 6. Weight of callus moieties immersed 24 hours in soap solution after completion of the drying cycle. Difference in per cent between moiety immersed in soap solution and moiety immersed in water as compared with original callus moiety weight. (Various commercial soaps coded C to K; drying time, 5 days)

soap solution than from the controls. On the other hand, with callus pieces immersed in soap solutions G, H, and K, it was found that after drying for 5 days, there was a slight weight gain as compared to the control. In these cases, there probably was absorption of soap constituents in the callus, compensating for the amounts of solubles which had been extracted.

Repetitive soaking of callus in soap solutions at room temperature provided the results shown in Table VII. The second immersion in soap solution did not cause additional weight loss.

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Table VII
Repetitive Sorption and Desorption of Callus Immersed in 20% Solutions of Soaps E, D, and K

Soap	Weight Loss[a] (%)		
	E	D	K
After 1st immersion of 21 hours	12.2	10.5	7.9
After 2nd immersion of 4 hours	11.1	10.4	3.1

[a] After 5 days' drying. All values based on original weight of particular callus piece.

Table VIII
Comparison of Weight Increases of Callus Moieties Immersed in Water and Hexylene Glycol[a]

Treatment	Swelling (%)	Dehydration (%)
Distilled water	97.0	34.9
Hexylene glycol (40% aqueous)	120.8	70.3

[a] Immersion for 1 hour, drying for 30 min.

Effect of Humectants

Hexylene glycol and polyethylene glycol were investigated alone and in combination with soap. Of two halves of a callus piece immersed for the same length of time (and dried for the same length of time), the one immersed in hexylene glycol solution retained water faster and for a longer time than the control (Table VIII).

It was found that callus halves immersed in a mixture of soap, hexylene glycol, and water also retain water faster and longer than the corresponding halves immersed in distilled water (Fig. 7).

When compared with the effect of soap alone, the humectant in combination with soap did not seem to have an additive effect. The humectant even decreased the amount of swelling and water absorption which was enhanced by soap. At a higher level of humectant, we observed less total absorption, but longer retention of water in the callus and apparently permanent retention of the humectant in the callus (Table IX).

Immediately following the 20 hours' immersion, the callus piece which was soaked in the mixture showed less weight gain than the control soaked in water. Throughout the drying stage, however, the callus piece which was immersed in the mixture showed a higher weight gain than the control.

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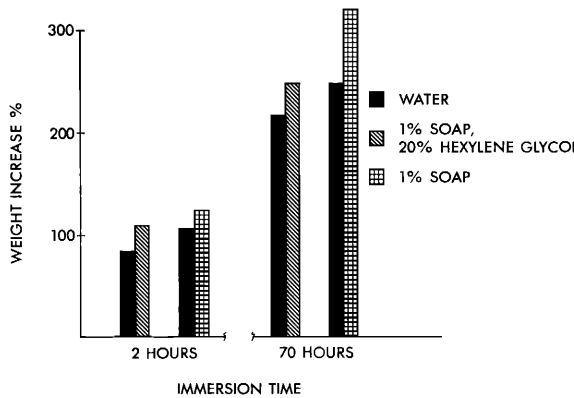

Figure 7. Weight increase *versus* immersion time for excised callus immersed in water, immersed in soap, and immersed in a mixture of 1% soap and 20% hexylene glycol in water

Table IX
Weight Increases of Callus Immersed for 20 Hours in Mixture of Soap, Hexylene Glycol, and Water, and Dried

	Weight Change[b] (%)		
Drying Time	5 min	4 hours	5 days
Water	226.0	4.4	−10.5
Mixture[a]	188.5	55.9	27.5

[a] 0.8% soap, 50% hexylene glycol, and 49.2% water.
[b] Minus sign indicates weight loss.

Table X
Influence of Humectant on the Water-binding Capacity of Stratum Corneum

	Weight Change[a] (%)		
Drying Time	5 min	70 min	5 days
	1st Immersion (5 hours)		
Water	153.5	0.9	−15.8
20% glycol	147.5	13.9	−4.1
50% glycol	34.5	8.3	−1.5
	2nd Immersion (4 hours)		
Water	123.0	−3.5	−29.8
20% glycol	117.0	0.6	−9.9
50% glycol	9.2	1.9	−7.8

[a] Of callus moieties immersed in distilled water and in polyethylene glycol. Minus sign indicates weight loss.

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The experiments with polyethylene glycol in water (Table X) showed that high amounts of this humectant reduce uptake of water by the callus piece and thereby restrict swelling, while at the same time soluble components were retained in the stratum corneum. The table shows weight changes of callus pieces immersed in water, immersed in a 20% solution of polyethylene glycol, and immersed in a 50% solution of polyethylene glycol. The results were similar to the ones obtained previously with a surfactant (Tween 80).

Conclusion

Use of callus is a fast screening method for the study of the effect of various compounds on ordinary skin, especially if one takes into consideration that there are differences in skin properties according to location on the body and the particular individual. It is assumed that the same chemicals, which have an effect on tough, hard callus, will behave similarly with thin stratum corneum.

Extension to wider ranges of concentration than usually investigated indicated that it is fallacious to make generalized conclusions from single concentrations. It was also shown that the water-binding properties of stratum corneum can be modified by water-soluble materials. Finally, when a mixture of compounds acts on stratum corneum, there is an interaction of these compounds as shown in the effect of soap and humectant on skin swelling in water.

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