The pH of the Stratum Corneum: An Update

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About 10 years ago, I attempted to explain some of the features of pH measurements on the skin's surface.[1] At that time, common knowledge accepted that alkaline substances, (soaps), applied to the skin might elicit adverse skin effects and that skin cleansing with neutral surfactants might be preferable.[2] Questions about this simplistic concept, pH dependence of skin irritation, are documented in the literature.[3] The picture was further obscured by the classical attribution of merits to the skin's so-called acid mantle. Since that time, investigators of skin physiology have avoided the controversy of potential skin damage by exposure to mildly alkaline substances. The most recent studies reported here describe newly discovered phenomena involved in pH changes during terminal differentiation, therefore, the earlier view is in need of updating.[1]

Generating water-soluble acids: The uncertainties of how the dermal pH, which is near 7, changes to the acidic pH, about 5, on the corneal surface have remained unanswered until now. This 100-fold increase in hydrogen-ion activity is today explained by the enzyme-controlled hydrolytic events in the epidermis, which generate several relatively strong, water-soluble acids. Among these are urocanic acid, pyrrolidone carboxylic acid, and perhaps lactic acid. (Lactic acid is known to be a sweat constituent; this might be the source for its presence in skin.) The fate of sulfuric or phosphoric acids in the stratum corneum (SC) is a mystery, although these acids must be formed during the disappearance of cholesteryl sulfate, or of the phosphatidic and nucleic acids.

The presence of pH-lowering acids in the SC is accepted today by all investigators and cannot be questioned.[4,5]

Recent Findings

About five years ago, Öhman and Vahlquist conducted measurements on the volar forearm of human subjects, determining the pH at different levels within the SC by stripping.[6] (The Volar forearm refers to the area above the wrist). They conducted similar experiments conducted on abdominal skin and on calf skin. For stripping, they used 3M

Table 1. Changes of surface pH as function of stripping

Male	Female	No. of tape strippings	No. of cyano-acrylate strippings
4.5	5.3	0	0
5.0	-	20	2
4.9	5.9	40	2
5.7	6.2	60	6
6.4	6.6	80	-
6.7	6.7	100	-
6.9	6.8	120	12

Ruban adhesive tape or cyanoacrylate resin. Tape stripping required 100-120 strippings, while cyanoacrylate stripping required only about 10 to 12 applications before the glistening layer was reached.

The recorded surface pH during stripping followed a sinoidal pattern, starting at pH 4.5 in males and at 5.3 females. Some of the data are shown in Table 1. After extensive stripping, transpidermal water loss (TEWL) in human subjects reached about 140g/$m^{2/}$. TEWL returned to normal levels (approx. 15 g/m^2/h) seven or eight days after stripping, but the pH on the skin surface remained elevated for at least another four to six days.

The upward shift in pH occurs rapidly after about 1/2 of the SC has been removed by stripping. After about 90 tape strippings, corresponding to removal of about 75% or more of the stratum corneum, the pH remains quite constant, slowly approaching the physiological pH.

Enzymatic processes: The sud-

Key words

Stratum corneum, pH variation, filaggrin, water-soluble acids

Abstract

The pH gradient results from enzymatic processes within the SC's major acidic skin components. The lowered pH near the skin's surface contributes to desquamation and lipid processing.

Der pH-Wert der Hault fällt von den inneren zu den äußeren Schichten des Stratum Corneums (SC) stark ab. Enzymatische Prozesse stellen die wichtigsten säurebildenden Hautbestandteile der mittleren Schichten des SC dar.

Le pH de la peau diminue très sensiblement des couches les plus profondes aux plus superficielles du Stratum Cornéum (SC). Des processus enzymatiques produisent la majorité des composants acides de la peau présents dans les couches médianes du SC.

El pH de la piel disminuye abruptamente desde las capas más internas hacia las más externas del estrato córneo (SC). Los procesos enzimáticos forman los principales componentes acídicos de la piel en las capas centrales del SC.

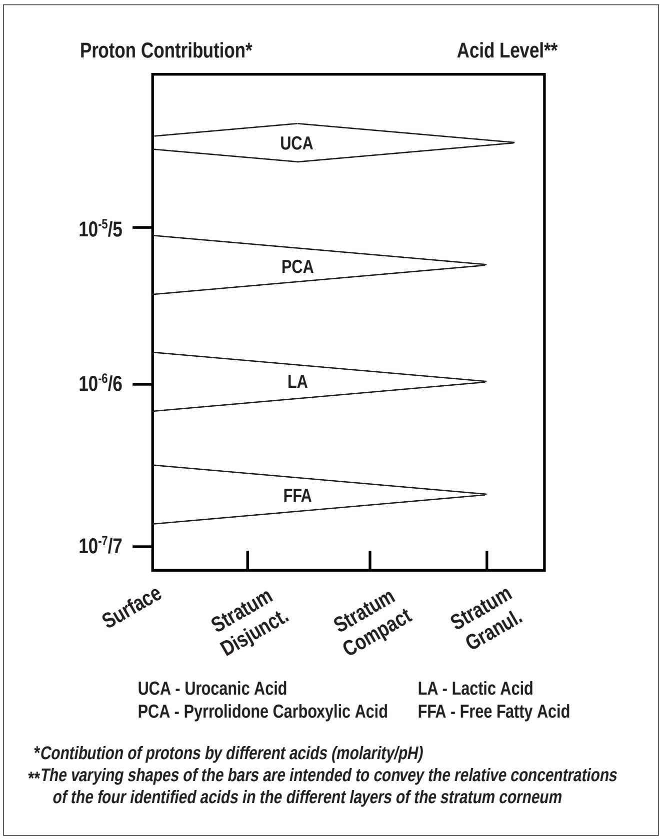

Figure 1. Sketch of acids found in human SC (after Öhman and Vahlquist[8])

den change in pH of about 2 units between 40 and 90 tape strippings is, in the authors' words, dramatic. They attribute this phenomenon to enzymatic processes occurring within the stratum corneum.

These results are confirmed by the data of Turner et al., who experimented with hairless mice. The increase in pH these researchers found during stripping with 3M Scotch #845 Book Tape was less dramatic than that observed by Öhman and Vahlquist. Not unexpectedly, Turner et al. also reported that the TEWL increased steadily as SC was removed.[6,7]

In a second study of intracorneal pH variation, Öhman and Vahlquist investigated whether ichthyosis, presumed to be a defect in desquamation, might also be the result of intracorneal pH defects.[8] The results showed that the intracorneal pH of subjects with ichthyosis vulgaris was almost identical with that of normal skin. The intracorneal pH changes in X-linked recessive ichthyosis, however, varied much more slowly as the viable epidermis was approached. This suggests that patients with X-linked recessive ichthyosis might suffer from some unexplained enzymatic deficiency.

Öhman and Valhquist provide an interesting hypothesis for the formation of the acids responsible for the low skin-surface pH in normal skin. A simplified sketch, based on their publication, is shown above.[8]

Filaggrin proteolysis: The authors suggest that the pH on the skin's surface can be attributed to sebum and other secretions (sweat) and the hydrolytic products derived from filaggrin proteolysis. In normal skin, cholesteryl sulfate disappears at the level of the SC; however, it persists into the upper levels of the SC in X-linked recessive ichthyosis. I note with interest that these authors do not attribute significant pH-lowering powers to the presence of free fatty acids on the skin surface.[8] Recognition of this fact is long overdue; it is readily explained by the very low solubility of typical fatty acids in water.

The uncertainties about the fates of sulfuric or phosphoric acids in the corneal layers remain. Öhman and Vahlquist suggest that cholesteryl sulfate is absent in the layers of the SC above the compactum layer. Unfortunately, the sulfur assays by Von Zglinicki et al. cannot be used to support this suggestion because of the proteinaceous constituents of the corneal cells are likely to contribute to the sulfur levels throughout the strateum corneum.[9]

Phosphorous is recycled: In contrast, the phosphorus levels show the expected drop between the stratum spinosum and the corneal layer.[9,10] The phosphorus content of the SC is remarkably low. This is attributed by Warner et al. to the likelihood that phosphorus is recycled during the degradation of nucleic acids and phospholipids.

Closing Comment

The low pH on the skin's surface has historically been viewed as a defensive mechanism against invading microbiota. The remarkable data showing a sudden pH change across the depth of the SC suggest a second mode of activity. The ultimate ripening of corneal cells and their desquamation appear to depend on hydrolytic processes which require a low pH. In this context, it is appropriate to ask whether the presence of hydroxy acids in the corneal layers might play a role in the normal development of the skin simply by lowering the pH.

The effects of water and topical (cosmetic) ingredients on the hydrolytic, lipolytic and desquamatory processes within the SC remain unexplained. In a publication by Rawlings et al., it is reported that glycerin was found 'superior to all other humectants and polyols' in an in vitro SC extensibility model. The enhancement of proteolysis by aqueous glycerin not only confirms earlier studies, but suggests that some cosmetic ingredients applied in skin care products might have detrimental effects on enzymatic processes in the corneal layers.

[a] *R. Lieckfeldt et al, Pharm Res.,* **12***, 1614-1417, 1995*
[b] *T Mauro, et al., Abstract 796, J. Invest. Dermatol.,* **104,** *687, 1995.*

The pH gradient observed in human epidermis may also play a critical role in the creation of a “good” skin surface via lipi modification. Thus, the free fatty acids creating a hydrophobic skin surface are likely to be present as neutralized salts in the viable epidermis. In addition, the formation of ceramides from glucosylceramides is controlled by β-glucocerebrosidase, which exhibits a distinct acidic pH optimum.[b] These pH effects help to establish a mechanism for the reason that soaps were recognized as irritating in normal use many years ago.

Summary

The low pH on the SC's surface comes primarily from the presence of water-soluble acids (urocanic, pyrrolidone carboxylic and lactic). The source of these acids is in all probability filaggrin, which is enzymatically degraded within the SC. The low skin-surface pH is probably not a result of the presence of sulfuric or phosphoric acids, and fatty acids seem to play only a minor pH lowering role.

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