MONOGRAPH:

Care for the Stratum Corneum & its pH

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The Skin as Liminal Space between our internal and external worlds

Our skin is the largest organ in our body, and it is a dynamic complex living system.

It is a thriving host of a constant flux of processes: sensing the world "outside" while monitoring the world "inside",

interfacing with our socio-cultural landscapes and with each other, while keeping an assortment of pathogens at bay,

self-modulating and producing chemicals endogenously, while connecting us with the rest of our cells and ourselves…

It is indeed, easy to imagine our skin as "just" a thin and shallow stretch of human tissue.

But the skin is astoundingly more and "deeper" than that.

The skin is quite the charmed cosmic, biochemical, socio-cultural and neuro-immunological space. For example, melanin (pigmentation) formation in our skin evolved as response to and interaction with the sun's ultraviolet UV solar radiation regimes.

And our skin and its typology or its perceived color has become a fundamental element in forming our sociocultural, ethnic, and political identities.

Indeed, our skin is the threshold of our internal and external worlds. It is a frontier space and a connective matrix, of our individuality, health, and ecology all at the same time.

And here, in this liminal space, we hope to discover our sense of wholeness, fluidity, and our wellbeing.

I. The Strata (layers and sublayers) of the Skin

Within the very outer layer of our skin, called the epidermis, are sublayers called "Stratum" (*Strata* – plural form). The outermost of which is called the "Stratum corneum", named after the horn-like structures and cells that make it.

The Stratum corneum is the most superficial layer --- that, which connects us to "the rest of the environment". The Stratum corneum acts as a dynamic protective barrier, coupled and embedded with immune system agents and responses that work in and through the other layers or strata of the skin.[1]

The stratum corneum can be likened to a battlefield of biological and chemical assaults and processes. Its physical terrain is composed of:

a) *Corneocytes* – "unnucleated and flattened keratinocytes" that are likened to "bricks" linked through an adhesive zone of cell membranes called desmosomes

b) *Intercellular lipids* – these are the "mortar" of lipids and ceramides that keeps the bricks together

Each of these components has unique interrelated functions. The A) corneocytes act as rigid barriers and produce hygroscopic molecules (water attracting things also referred to as "Natural Moisture Factors" or NMF).

And the B) inter-cellular lipids seal and keep the moisture in to prevent drying, i.e. "Trans-epidermal water loss" or TEWL.[2]

II. The Importance of **pH** in the Stratum corneum

One of the most crucial early discoveries is that the stratum corneum's functions are mediated by **pH**.

*[**pH** = the concentrations of [Hydrogen ions +] vs pure water]*

The more H+ ions and higher concentration of H+ ions, the lower pH = acidic. The pH of the pure water is 7.0; human blood pH is 7.4; and the pH of intercellular water is around 6.8.

In the early 19th Century, the most superficial skin layer was first described and termed as "the acid mantle" (*Sauermantels* in

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[1] Schulz *etal* (2019) "Neutrophil Recruitment to Non invasive MRSA at the Stratum Corneum of Human Skin Mediates Transient Colonization", Cell Reports

[2] Sevrein and Bronte (2007) "Skin Hydration: A Review", Journal of Cosmetic Dermatology

Deutsche) because of its **pH levels of 5.0 - 5.5** (slightly acidic pH).[3] This slightly acidic pH level is found to be most optimal for the functions of the stratum corneum.

An increased pH of the stratum corneum is associated with skin pathologies such as eczema, acne, ichthyosis vulgaris etc. [4] Atopic Dermatitis is increasingly affecting children around the world, and can be progressive (also referred to as the "atopic cascade") in its negative health impacts i.e development of allergic rhinitis later in adulthood. [5]

III. Soaking, Washing and other Assaults on the Stratum corneum

Soaps, scrubs, alcohol-based sanitizers, or detergents or soak in hot tubs, swimming pools strip our stratum corneum of the natural moisturizing factors (NMF) that are innately produced by the skin; and contribute to an increase **pH** in the stratum corneum.

When the stratum corneum is stripped of the NMF, our skin feels dry and flaky and its integrity is compromised. Thus, the skin becomes susceptible to infection and attacks by pathogens and allergens.

Even just soaking our skin in pure water, the stratum corneum layer can be substantially stripped of its components.[6] When we bathe in hot water, or swim in pools, our stratum corneum's Natural Moisturizing Factors can also be diminished. Moreover, some studies have found that the skin is able to replenish the stratum corneum in approximately four (4) hours.

IV. Skin Toning Strategy – An essential step

To aid in buffering and correcting the stratum corneum to a lower or acidic pH, a neutralizing and acidifying skin toner product can be helpful. The toning system that have been formulated by the S.P.A. AQUA PRIMA, under the brand name, "STRATAGEM Skin Care" is formulated to aid pH balancing and buffering on the stratum corneum. The "Essential Moisturizing Toner" is an essential step in personal skin care routine especially after skin cleansing.

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[3] Surber etal. (2018) "Acid Mantle: A Myth or an Essential Part of Skin?", Current Problems in Dermatology

[4] Rippke etal. (2004) "Stratum corneum pH in atopic dermatitis: impact on skin barrier function and colonization with Staphylococcus Aureus", American Journal of Clinical Dermatology

[5] Bell and Brown (2017) "Atopic eczema treatment now and in the future: Targeting the skin barrier and key immune mechanisms in human skin", World Journal of Dermatology

[6] Robinson (2010) "Natural Moisturizing Factor in the SC 2: Regeneration of NMF over time", Journal of Cosmetic Science

The key ingredients include botanical extracts and essential oils from various regions around the world i.e. Seabuckthorn, *Hippophae rhamnoides* Kakadu plum, *Terminalia Ferdinandiana* which provide sources of Vitamin C and antioxidants that are so beneficial for skin repair[7]. These botanical extracts are further enhanced by other advanced + proprietary + clinically tested compounds and ingredients. *[International Nomenclature of Cosmetic Ingredients (INCI) List below.]*

Designed to be applied topically (facial or body skin regions), the "Essential Moisturizing Toner" is designed to provide immediate relief for the stratum corneum through mild acids (i.e. Vitamin C), humectants that attract water from the environment; and through emollients (oils) thereby supporting the conditions for natural recovery of the stratum corneum's Natural Moisturizing Factors, and preventing Trans-epidermal water loss.

V. Essential Moisturizing Toner Ingredients' and Proposed Mechanisms of Actions

Vitamin C from the botanical extracts of Kakadu plums and Seabuckthorn berry oil provide the acidity factor to reduce the pH of the stratum corneum. Hyalauronic acid is included in the Essential Moisturizing Toner as the primary humectant.

Fatty acids present in Seabuckthorn berry oil, e.g. phenolic acid and ferulic acid used to reduce the Trans-epidermal Water Loss. Ferulic acid in conjunction with Vitamin C has been found to be effective in reducing UV damage on the skin. [8]

Gamma-Linoiec Acid (GLA) found in Seabuckthorn berry oil is reported to get converted into prostaglandins that aid in anti inflammatory, anti infection responses in the subdermal layers of the skin. Omega 7, one of the abundant active in Seabuckthorn berry oil encourages cell regeneration and regulates functions of skin's sebaceous glands.

Palmitic and stearic acids, works as protective occlusion of the skin barrier and linolic acid strengthens the lipid barrier, and regulates skin metabolism. It is reported that Seabuckthorn berry oil as a strong antioxidant that can be helpful for eczema symptoms reduction.

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[7] Pumori, S. (2013) "Vitamin C in Dermatology", Indian Dermatology Online Journal

[8] Pumori, S. (2013) "Vitamin C in Dermatology", Indian Dermatology Online Journal

An Essential Hydrating Skin Toner

Ingredients Presented by

Aqua,

Glycerin,

Glyceryl Stearate Citrate,

Carya Ovata Bark Extract,

Terminalia Ferdinandiana Fruit Extract,

Retinyl Palmitate,

Tocopherol,

Hippophae Rhamnoides (Sea Buckthorn) Fruit Oil,

Citrus Sinensis (Sweet Orange) Peel Oil,

Citrus Paradisi (Pink Grapefruit) Peel Oil,

Coconut Flavour (Aroma),

Xanthan Gum,

Citrus Nobilis (Clementine) Peel Oil,

Vanilla Flavour (Aroma)

PERSONAL ANECDOTE:

"After spending hours in a salt water therapy pool, the Essential Hydrating Toner has provided instant and cumulative relief and resilience for my skin. I have noted the decreased cracking and long-lasting suppleness and a sense of structural integrity (sometimes even without using lotions) of my skin even after extended work time in the pool with my patients."

"Advocating for the Stratum corneum pH seems to be a logical approach to support skin resilience. The Essential Hydrating Skin Toner Mist and the Essential Moisturizing Lotion have cleared all the Standard cosmetic Stability and Microbiology Challenge Tests."

Bibliographic Notes:

1) Pumori, S. (2013) "Vitamin C in Dermatology", Indian Dermatology Online Journal, 2013 Apr-Jun; 4(2): 143–146.: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC3673383/

"Vitamin C: antioxidant/ slows photoaging damage + collagen synthesis + anti-inflammatory properties + depigmenting agent + stable with Vit E and Ferulic Acid. A combination of 0.5% ferulic acid (a potent antioxidant of plant origin) with 15% Vit. C and 1% Vit. E can increase the efficacy of Vit. C eight-fold" (Farris PK. Cosmetical Vitamins: Vitamin C. In: Draelos ZD, Dover JS, Alam M, editors. Cosmeceuticals. Procedures in Cosmetic Dermatology. 2nd ed. New York: Saunders Elsevier; 2009. pp. 51–6) in "Vitamin C as antioxidant against photoaging; important to deliver into the dermis."

2) Al-Niaimi, F. and Chiang, N. (2017) "Topical Vitamin C and the Skin: Mechanisms of Action and Clinical Applications", Journal of Clinical and Aesthetic Dematology, J Clin Aesthet Dermatol. 2017 Jul; 10(7): 14–17: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5605218/

"As one of the most powerful antioxidants in the skin, vitamin C has been shown to protect against photoaging, ultraviolet-induced immunosuppression, and photo-carcinogenesis. It also has an antiaging effect by increasing collagen synthesis, stabilizing collagen fibers, and decreasing collagen degradation. It decreases melanin formation, thereby reducing pigmentation. Vitamin C is the primary replenisher of vitamin E and works synergistically with vitamin E in the protection against oxidative damage."

"Topical vitamin C has a wide range of clinical applications, from antiaging and antipigmentary to photoprotective. Currently, clinical studies on the efficacy of topical formulations of vitamin C remain limited, and the challenge lies in finding the most stable and permeable formulation in achieving the optimal results."

3) *Pinnell SR, Yang H, Omar M, Monteiro-Riviere N, DeBuys HV, Walker LC, Wang Y, Levine M, (2001)* Topical L-ascorbic acid: percutaneous absorption studies in Al-Niami and Chiang (2017) *Dermatol Surg. 2001 Feb; 27(2):137-42.d: https://pubmed.ncbi.nlm.nih.gov/11207686/*

"Reducing the acidity of L-ascorbic acid to a pH below 3.5 is an effective method of improving its stability and permeability. This has shown to greatly aid its penetration, largely because of the transformation from the charged to the uncharged form of the molecule."

4) Rippke etal. (2004) "Stratum corneum pH in atopic dermatitis: impact on skin barrier function and colonization with Staphylococcus Aureus", American Journal of Clinical Dermatology, 2004;5(4):217-23. doi: 10.2165/00128071-200405040-00002: https://pubmed.ncbi.nlm.nih.gov/15301569/

"Growing evidence suggests an impaired release of proton donors, such as amino acids, urocanic acid, and lactic acid, to the stratum corneum in atopic dermatitis, as a result of reductions in filaggrin proteolysis and sweat secretion. In addition, an impaired formation of free fatty acids from sebaceous lipids and epidermal phospholipids seems to be involved. Because both lipid organization and lipid metabolism in the stratum corneum requires an acidic pH, these alterations might contribute to the disturbance of skin barrier function observed in atopic dermatitis. Furthermore, bacterial growth and virulence of S. aureus, as well as defensive host mechanisms, have increasingly been delineated as pH dependent, giving rise to a new understanding of the pathophysiology underlying increased skin colonization seen in atopic dermatitis."

5) Sevrein and Bonte (2007) "Skin Hydration: A Review", Journal of Cosmetic Dermatology https://pubmed.ncbi.nlm.nih.gov/17524122/

"Water is absolutely essential for the normal functioning of the skin and especially its outer layer, the stratum corneum (SC). Loss of water from the skin must be carefully regulated, a function dependent on the complex nature of the SC. The retention of water in the SC is dependent on two major components: (1) the presence of natural hygroscopic agents within the corneocytes (collectively referred to as natural moisturizing factor) and (2) the SC intercellular lipids orderly arranged to form a barrier to trans-epidermal water loss (TEWL). The water content of the SC is necessary for proper SC maturation and skin desquamation. Increased TEWL impairs enzymatic functions required for normal desquamation resulting in the visible appearance of dry, flaky skin. There have been recent discoveries regarding the complex mechanisms of skin hydration. In particular, it has been discovered that glycerol, a well-known cosmetic

ingredient, exists in the SC as a natural endogenous humectant. Hyaluronan, which has been regarded mainly as dermal component, is found in the epidermis and is important for maintaining normal SC structure and epidermal barrier function. More importantly, the discovery of the existence of the water-transporting protein aquaporin-3 in the viable epidermis and the presence of tight junction structures at the junction between the stratum granulosum and SC have brought new insights into the mechanisms of skin water distribution and barrier function."

6) Robinson *etal* (2010) "Natural Moisturizing Factor in the SC 1: Effects of Lipid Extraction and Soaking", Journal of Cosmetic Science

https://pubmed.ncbi.nlm.nih.gov/20211113/#:~:text=Abstract,hygroscopic%20molecules%20including%20amino%20acids

"Natural moisturizing factor (NMF) is essential for appropriate stratum corneum hydration, barrier homeostasis, desquamation, and plasticity. It is formed from filaggrin proteolysis to small, hygroscopic molecules including amino acids. HPLC results were standardized to the amount of protein removed by the tapes. An increase in NMF was found with increased SC depth. Also, the combination of extraction and soaking was found to increase NMF loss relative to control or to extraction or soaking alone. Our results indicate that common skin care practices significantly influence the water binding materials in the upper SC. The findings have implications for the evaluation and formulation of skin care products."

7) Robinson etal (2010) "Natural Moisturizing Factor in the SC 2: Regeneration of NMF over
Time", Journal of Cosmetic Science
https://pubmed.ncbi.nlm.nih.gov/20211114/

"Significant decreases in NMF levels, quantified by HPLC analysis of serial tape strips, were observed 0.5 hours after soaking, with a replacement of NMF occurring by the four-hour mark. This replacement corresponds to a parallel rebound in skin pH also observed at these times.

In addition, significant increases in skin pH were observed during the immediate post-soak period. These findings suggest that short-term exposure to water alone produces significant changes in the stratum corneum."

8) Crowther *etal* (2008) "Measuring the effects of topical moisturizer on stratum corneum thickness, water gradients and hydration in vivo", British Journal of Dermatology,
https://pubmed.ncbi.nlm.nih.gov/18616783/

"In vivo CRS was validated as a technique to measure SC thickness on both palmoplantar and, particularly, on non-palmoplantar skin sites. (ii) Moisturizers improve skin moisturization but in this study only formulation A improved SC thickness, water gradients and hydration as measured by CRS. We hypothesize that this was due to compositional differences between the products. We believe that niacinamide (nicotinamide, vitamin B(3)) is probably contributing significantly to this effect, as it has been proven to increase epidermal lipogenesis and SC barrier function in other studies."

9) Zielinska and Nowak (2017) "Abundance of Active Ingredients in Seabuckthorn Oil", Lipids in Health and Disease 2017; 16: 95.: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC5438513/

"Moreover, its unique unsaturated fatty acids, such as palmitooleic acid (**omega-7**) and gamma-linolenic acid (omega-6), give sea-buckthorn oil skin regeneration and repair properties. Sea-buckthorn oil also improves blood circulation, facilitates oxygenation of the skin, removes excess toxins from the body and easily penetrates through the epidermis. Because inside the skin the gamma-linolenic acid is converted to prostaglandins, sea-buckthorn oil protects against infections, prevents allergies, eliminates inflammation and inhibits the aging process. With close to 200 properties, sea-buckthorn oil is a valuable addition to health and beauty products."

10) Peter, E. (2015) "Stratum corneum Acidification, How and Why?" Experimental Dermatology, PMC 2015 Aug 28: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4552322/

"Three Functions of the Acid Mantle: 1) Antimicrobial and epidermal permeability barrier homoeostasis 2) SC integrity and resistance to stripping + SC cohesion (degradation by kallikrein KLK) + desquamation 3) Pro inflammatory cytokine activation, increased pH increases KLK activity that trigger cascade of inflammatory response. While repeated insults lead to inflammation, single perturbations instead unleash beneficial, cytokine-initiated, homoeostatic responses (e.g. accelerated DNA and lipid synthesis) that help to restore barrier homoeostasis"

11) Schulz *etal* (2019) "Neutrophil Recruitment to Non invasive MRSA at the Stratum Corneum of Human Skin Mediates Transient Colonization", Cell Reports, https://www.x-mol.com/paper/5921989

"*Staphylococcus aureus* is a leading cause of skin and soft issue infection, but paradoxically, it also transiently, and often harmlessly, colonizes human skin.

An obstacle to understanding this contradiction has been a shortage of *in vivo* models reproducing the unique structure and immunology of human skin. In this work, we developed a humanized model to study how healthy adult human skin responds to colonizing methicillin-resistant *S. aureus* (MRSA).

We demonstrate the importance of the outer stratum corneum as the major site of bacterial colonization and how noninvasive MRSA adhesion to corneocytes induces a local inflammatory response in underlying skin layers. This signaling recruits neutrophils to the skin, where they control bacterial numbers, mediating transiency in colonization.

This work highlights the spatiotemporal aspects of human skin colonization and demonstrates a subclinical inflammatory response to noninvasive MRSA that allows human skin to regulate the bacterial population at its outer surface."

12) Schmid-Wendtner and Korting, (2006) "The pH of the Skin and barrier function", Skin Pharmacology and Physiology 2006;19(6):296-302. doi: 10.1159/000094670. Epub 2006 Jul 19.: https://pubmed.ncbi.nlm.nih.gov/16864974/

"The skin pH is affected by a great number of endogenous factors, e.g. skin moisture, sweat, sebum, anatomic site, genetic predisposition and age. In addition, exogenous factors like detergents, application of cosmetic products, occlusive dressings as well as topical antibiotics may influence the skin pH. Changes in the pH are reported to play a role in the pathogenesis of skin diseases like irritant contact dermatitis, atopic dermatitis, ichthyosis, acne vulgaris and Candida albicans infections. Therefore, the use of skin cleansing agents, especially synthetic detergents with a pH of about 5.5, may be of relevance in the prevention and treatment of those skin diseases."

13) Haftek, M. (2015) "Epidermal barrier disorders and Corneodesmosome defects", Cell Tissue Research 2015; 360(3): 483–490.: https://www.ncbi.nlm.nih.gov/pmc/articles/PMC4452581/

"Corneodesmosomes are modified desmosomes present in the stratum corneum (SC). They are crucial for SC cohesion and, thus, constitute one of the pivotal elements of the functional protective barrier of human skin. Expression of corneodesmosomes and, notably, the process of their degradation are probably altered during several dermatoses leading to the disruption of the permeability barrier or to abnormal, often compensative, SC accumulation. These different situations are reviewed in the present paper.

Inflammatory diseases, including atopic dermatitis, psoriasis, and acne vulgaris, which show an increased pH should probably also have reduced buffer capacities. For the treatment of the skin diseases and in aged skin,

emollient with a pH that is slightly more acidic than the average normal pH and an appropriate buffer capacity should be preferably used."

14) Proksch, E. (2018) "Buffering Capacity", Current Problems in Dermatology. 2018; 54:11-18. doi: 10.1159/000489513. Epub 2018 Aug 21: https://pubmed.ncbi.nlm.nih.gov/30130768/

"Each biological system possesses a widely unrecognized buffer system to maintain acid-base balance to a specific pH. Our lives are dependent on the functioning of buffer systems. A buffer system is a solution that resists a change in pH when acids or bases are added. The skin possesses a fairly high buffer capacity, which is determined by the amount of H+ or OH- ions that is needed until the pH value of a solution changes by the unit 1. Buffers contain a weak or medium strong acid (base) and the corresponding salt. Buffers that show a pKa in the range of the Stratum corneum surface pH are most important for the skin. Buffer capacity is reduced both in baby skin and in aged skin. External factors, water, and detergent may reduce the local buffer capacity because of the elution of buffer chemicals leading to increased pH and irritative contact dermatitis. Inflammatory diseases, including atopic dermatitis, psoriasis, and acne vulgaris, which show an increased pH should probably also have reduced buffer capacities. For the treatment of the skin diseases and in aged skin, emollient with a pH that is slightly more acidic than the average normal pH and an appropriate buffer capacity should be preferably used."

15) Bell and Brown (2017) "Atopic eczema treatment now and in the future: Targeting the skin barrier and key immune mechanisms in human skin", World Journal of Dermatology, Aug 2, 2017; 6(3): 42-51, https://www.wjgnet.com/2218-6190/full/v6/i3/42.htm

"The skin facilitates a number of key roles but its functioning can be impaired by disease. Atopic eczema is a chronic inflammatory disease where the skin barrier has become leaky, and inflammation occurs. It affects up to 20% of children and 3% of adults worldwide, manifesting as red itchy patches of skin with varying severity.

This review aims to investigate the leaky skin barrier and immune mechanisms from the perspective of potential novel treatments. The complexity of atopic eczema as a disease is what makes it difficult to treat. Genome-wide association studies have highlighted possible genetic variations associated with atopic eczema, however in some cases, individuals develop the disease without these genetic risk factors.

Loss of function mutations in the filaggrin gene are one of these associations and this is plausible due to its key role in barrier function. The Th2 immune response is the link with regards to the immune mechanisms

as atopic inflammation often occurs through increased levels of interleukin (IL)-4 and IL-13. Eczematous inflammation also creates susceptibility to colonisation and damage by bacteria such as Staphylococcus aureus.

Potential novel treatments are becoming ever more specific, offering the hope of fewer side effects and better disease control. The best new treatments highlighted in this review target the immune response with human beta defensin 2, phosphodiesterase-4 inhibitors and monoclonal antibodies all showing promise."

16) Surber etal. 2018 "Acid Mantle: A Myth or an Essential Part of Skin?", Current Problems in Dermatology 2018;54:1-10. doi: 10.1159/000489512. Epub 2018 Aug 20.: https://pubmed.ncbi.nlm.nih.gov/30125885/

"For many more biochemical processes within the skin, the compartmental pH is crucial, for example, in pigmentation, ion homeostasis, epidermal (stem) cell behavior, and so on. The often existing difference between the H+ concentration of extra- and intracellular as well as subcellular compartments establishes an ionic, electric, and/or osmotic driving force; hence, H+ concentration per se acts as an extra-, intra,- and subcellular signaling modality affecting and controlling many cellular functions. One may even consider pH a universal signal and effector. It is therefore also no surprise that skin pH shifts have been observed in various skin pathologies. More recently, in carefully controlled trials (acne, atopic dermatitis, incontinence-associated dermatitis, aged skin), the benefits of targeted skin acidification have become evident and the use of topical preparations with reduced pH may be recommended."

17) Web resource: Active Ingredients of Ginger Lily Oil: https://www.bloomingoils.com/Ginger-Lily-Essential-Oil

"Linalool, (E)-Isoeugenol, Indole, Methyl benzoate, Valeric acid, Jasmine lactone, Benzyl benzoate, Methyl jasmonate, B-Caryophyllene, Methyl epi-jasmonate, Eugenol, Benzyl cyanide, 1,8-Cineole, (Z)-Jasmone, B-Ocimene, Phenylacetaldehyde, (E,E)-2,6,10-trimethyl-2,6,10,12-tridecatetraene."