J. Cosmet. Sci., 53, 229–236 (July/August 2002)

Glycerin (glycerol): Current insights into the functional properties of a classic cosmetic raw material

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Accepted for publication March 15, 2002.

INTRODUCTION

Glycerin was discovered in the late 18th century by Carl Wilhelm Scheele (1742–1786) and has had over a century of use in cosmetic and personal care products. The primary features that account for its numerous uses are based upon its humectant or hygroscopic properties, solubility characteristics similar to water, its inherent lubricity, and glycerin's capacity to prevent freezing and promote product shelf life. It is also a natural constituent of plants and is involved in physiological and biochemical processes (1).

The beneficial cosmetic attributes of glycerin have been recognized for over 75 years. However, our understanding of the diverse mechanisms by which glycerin influences skin moisturization, accelerates healing, improves barrier properties, smoothes the skin surface, etc., had been limited up until the late 1970s. The purpose of this review article is to present an overview of recent research findings that provide a broader understanding of glycerin's multi-dimensional functionalities.

A brief summary of the classic supportive literature for the above properties is provided; however, the primary objective of this review article is to describe the biological functionalities of glycerin that have been discovered within the past twenty-five years. (Since glycerin is frequently referred to as glycerol in the scientific literature, the two descriptors are used interchangeably in this review.)

Glycerin is recognized as an effective over-the-counter (OTC) skin protectant when used at 20% to 45% in skin products (2). The OTC panel did not consider undiluted glycerin to be effective as a skin protectant. Undiluted glycerin can actually serve to dehydrate skin, based upon osmotic action. It has been demonstrated by numerous methods to be an effective moisturizer and skin conditioner when used at levels above 3%, although the choice of vehicle can influence performance.

Table I, (3) shows the comparative per cent moisture holding ability of selected natural humectant materials at room temperature (RT) and 65–70% relative humidity (RH).

In a study by Deshpande *et al.* (4), raw materials, contained in standard petri dishes, were evaluated at 20% RH over a saturated solution of potassium acetate. This RH value was

Table I
Moisture Holding Ability of Selected Natural Humectants (% at RT, 65–70% RH)

Material	1 Day	5 Days
Sodium lactate	90%	25%
Sodium PCA	70%	30%
Glycerin	50%	5%
Protein hydrolyzate	20%	10%
Sodium hyaluronate	388%	98%

maintained within (±) 2% for the length of the study. Results showing the comparative superiority of glycerin at this low RH condition are summarized in Table II.

The researchers emphasized the need for agents that function effectively as humectants at a relative humidity of 20%. Only two compounds out of numerous materials tested, glycerin and sodium capryl lactylate, showed any appreciable activity at this humidity, which is often encountered in unhumidified indoor environments during winter.

The *in vitro* data shown in Tables I and II do not correlate with the capacity of these materials to perform *in vivo.* The high molecular weight and ionic charge of the materials listed, with the exception of glycerin, limit their capacity to penetrate skin and to perform effectively. Research studies (11,12) presented in this review will document glycerin's capacity to penetrate skin and create a "reservoir."

Studies conducted within the past twenty years have been conducted *in vivo* with the aid of equipment and techniques that have been continuously refined. Research by both university and corporate R&D teams has enabled us to gain significant understanding of the complex interactions of glycerol with the epidermis.

Results of some of these interactions, listed below, are supported by studies published within the past 25 years. Interaction of glycerol with the epidermis:
1. increases extensibility of the stratum corneum
2. increases the water gradient in the skin
3. reduces surface roughness (may not be caused solely by moisturization)
4. penetrates into the phospholipid bilayers
5. maintains the intercellular lipid cement in a fluid liquid crystal state, particularly under conditions of low temperature and low RH
6. accelerates recovery of barrier function *in vivo*

Table II
Percentage of Moisture Absorbed or Regressed (*) at 20% Relative Humidity

Material tested	Day 1 (%)	Day 5 (%)	Day 11 (%)	Day 15 (%)
Glycerin	9.00	6.13	5.19	4.91
Sodium PCA (50%)	23.03*	36.48*	38.61*	39.04*
Sodium lactate (60%)	3.05*	19.06*	27.36*	28.87*
Methyl gluceth-10	0.43	0.42	0.24*	0.43*
Methyl gluceth-20	0.87	1.46	1.36	1.33
Sodium capryl lactylate	2.19	2.74	2.24	2.12

7. serves to accelerate wound healing
8. aids in the digestion of desmosomes
9. provides a skin protection function
10. enhances corneocyte desquamation
11. does not interfere with biochemical processes in the skin

To provide the physiochemical and biochemical basis for the above functionalities of glycerin, reference to a series of seminal scientific papers will be made.

EARLIER STUDIES

A stereomicroscopic test for moisturizing efficacy (5) developed by Highley *et al.* is based upon the ability of moisturizers to prevent or alleviate soap-induced dry skin by using the back of the hand as a substrate. One of the advantages of this procedure is that it permits comparative efficacy measurements on moisturizing preparations regardless of their form or water content. Another advantage is that by means of this test using panels of small size, information is generated, which could otherwise be obtained only through clinical testing on large populations.

A numerical grading system for relative skin dryness (70 to 80) was developed by means of which a numerical measure of moisturizing efficacy was obtained (differences of 30 to 40 between untreated and treated hands are rated as good). This technique clearly demonstrated that the use of 25% glycerol in water, over a period of four days, was distinctly superior to the use of similar solutions of both propylene glycol and sorbitol. The comparative effectiveness of these polyols is shown in Table III.

In a significant paper (6) published in 1984 by Bissett *et al.,* "Skin conditioning with glycerol," a human skin condition study conducted during winter (in Cincinnati, OH) using outside lower leg dry skin was reported. The panels consisted of male and female volunteers aged 25 to 55. One milliliter of test material was applied twice daily to an approximately 150-cm^2 skin area. All panelists used two test materials, one for each leg. Two trained graders using a 0–5 scale did visual grading of the skin. Panelists were allowed to continue their normal bathing/showering practices. Results after two weeks of testing are shown in Table IV.

Similar type *in vivo* studies conducted on dry pig skin showed similar efficacy as the glycerol concentration was increased up to 20%, beyond which increased concentration produced only a small additional benefit.

Several other polyols were tested (four weeks of treatment) as skin conditioners on dry

Table III
Effectiveness of Some Commonly Used Cosmetic Ingredients

	Stereomicroscope ratings by trained observers		
Ingredient tested	Treated hand	Untreated hand	Difference (untreated–treated)
Glycerin (25% in H_2O)	34	68	+34
Propylene glycol (25% in H_2O)	71	70	−1
Sorbitol (25% in H_2O)	73	87	+14

Table IV
Improvement in Human Dry Skin Condition by Various Concentrations of Glycerol

Treatment	Grade reduction[a] (skin improvement)
5% Glycerol	0.86
10% Glycerol	1.44
20% Glycerol	1.74
40% Glycerol	1.80

[a] Combined results (after two weeks of treatment) of three studies, no one study involving all treatments. Water was the control in all studies. Starting grade averages were 2.02 to 2.71.

pig skin to determine their effectiveness. Liquids such as propylene glycol and 1,3-propanediol (tested as 10% and 50% aqueous solutions) did not provide a skin-conditioning benefit. Aqueous solutions (10% and 50%) of crystalline polyols such as erythritol, xylitol, and sorbitol provided only a marginal benefit.

In the discussion section of the Bissett article, the researchers made the following comments: "The exact nature of glycerol's mechanism of action is not clear. Glycerol is a nonvolatile, hygroscopic liquid. These properties presumably allow it to retain water in the skin. The water-glycerol mixture then hydrates and plasticizes the skin to prevent dehydration and the resultant physical damage in a stressful environment. Immediately after application, glycerol also provides a masking of the scales on the skin surface. However, the benefit diminishes with time and is lost with washing. The long-term benefits of glycerol reported here are in the absence of this 'cosmetic cover-up.' Whether glycerol in the viable epidermis can also affect the generation of new stratum corneum is not known. Alteration of the course of tissue synthesis might result in a stratum corneum more resistant to dehydration."

This is a significant publication because the researchers thoroughly documented the skin conditioning properties of glycerin and presented insights concerning its potential mechanisms of action. Much of their insights are substantiated in later studies that are summarized in this review.

LATER STUDIES

With the use of sophisticated bioengineering equipment, Batt *et al.* (7) studied the changes in the physical properties of the stratum corneum following treatment with glycerol. Preparations containing the humectant were applied topically to the skin of young adults, and the physical effects on the stratum corneum were examined using instrumental techniques. The effects measured were reductions in transepidermal water loss and electrical impedance, smoothing of the skin surface profile, and an increase in the coefficient of friction. These effects were found to accompany an improvement in the expertly assessed condition of the skin. Found to last for periods in excess of eight hours, these effects were similar to those observed transiently after the topical application of water.

These researchers summarized their views in their 1988 article as follows: "The data reported are consistent with the hypothesis that the beneficial effects of glycerol on skin condition are due to its physical effects on the status of water in the outer layers of the stratum corneum. This may be the result of glycerol interactions with the stratum corneum lipid structures or proteins, altering their water-binding and/or hydrophilic properties." This hypothesis correctly anticipates research findings revealing the influence of glycerol on the lipid bilayer to be published within the next few years.

A paper published by Froebe (8) in 1990 reports the prevention of stratum corneum phase transitions *in vitro* by glycerol and describes this phenomenon as an alternate mechanism for skin moisturization.

Since intercellular lipids have an integral role in the barrier function of the stratum corneum, it had been proposed by Friberg and Osborne (9) that maintaining the lipids in a liquid state is required for optimal barrier function in preventing water loss. This research demonstrated that the addition of glycerol to a mixture of stratum corneum lipids *in vitro* inhibits the transition from liquid to solid crystals even when the water content is reduced by low ambient humidity (6% RH). Glycerol does not act as a humectant at 6% RH, either when tested alone or when incorporated into the model lipids. Therefore, the researchers concluded that in a dry atmosphere glycerol acts as a skin moisturizer by inhibiting the lipid phase transition from liquid to solid crystal, rather than by acting as a humectant. They claimed that this represents an alternate, more likely molecular mechanism of action for glycerol.

Further support for the above study and its conclusions are provided in an article by Friberg (10) entitled "Micelles, microemulsions, liquid crystals, and the structure of stratum corneum lipids." A phase diagram is included that shows the liquid crystal layered structure to be changed to a crystal structure when the water content is reduced below a certain level. This change is theorized to have a drastic effect, *in vivo,* on the appearance and smoothness of the skin.

An article by Rawlings (11) provides further support for glycerol's multidimensional activities. From these studies, it is proposed that the properties of glycerol as a humectant, occlusive, and as a lipid phase-modulating molecule, are likely to contribute to the improvements in stratum corneum desquamatory enzyme activities and desquamation itself. The researchers believe that one of the major beneficial actions of glycerol-containing moisturizers *in vivo* is to aid in the enzymatic digestion of superficial desmosomes in subjects with skin xerosis, thus improving the desquamatory process.

In a paper presented by Shapiro (12) at the First International Symposium on Cosmetic Efficacy, results of a five-day double-blind clinical study to determine the ultrastructural changes in skin following use of high-glycerin (25% and 40%) therapeutic moisturizers are presented. Test materials were applied to the volar forearms twice a day. Electron microscopic examination of stained punch biopsies of the test sites and untreated control site revealed that both high-glycerin products penetrated the entire thickness of the stratum corneum and provided expanded appearance, with no identifiable structural changes evident in deeper epidermal or dermal layers. Pure glycerin appeared to penetrate minimally and have little or no effect on the appearance of the stratum corneum.

The researchers stated that "bulking" of the stratum corneum with a glycerin reservoir, without disruption of the liquid crystal/lamellar structure, is believed to enhance the resilience of skin exposed to harsh climatic conditions and helps explain the sustained skin healing observed following use of these products. These studies also suggest a role for a well-formulated glycerol composition in normalization of barrier function that is essential in healing of dry skin and possibly wound healing.

RECENT STUDIES

Substantiation for glycerol's role in normalizing barrier function is supported by recent research (13) conducted by Fluhr *et al.* Two studies were performed to evaluate the influence of glycerol on the recovery of damaged corneum barrier function. Measurements of transepidermal water loss (TEWL) and capacitance were conducted in a three-day followup after tape stripping (study 1) and in a seven-day followup after barrier damage due to repeated washing with sodium lauryl sulfate (study 2).

In study 1, a faster barrier repair as measured by reduced TEWL was shown at the glycerol-treated sites. Significant differences between glycerol open vs untreated and glycerol occluded vs untreated were observed at day 3.

In study 2, a faster barrier repair was seen in glycerol-treated sites, with significant differences between untreated and base-treated sites seven days after the end of treatment. Stratum corneum hydration showed highest values in glycerol-treated sites after three days of treatment. Glycerol is claimed to create a stimulus for barrier repair and to improve stratum corneum hydration. Since the glycerol-induced recovery of barrier function and stratum corneum hydration were observed even seven days after the end of treatment, the researchers regard glycerol as a barrier stabilizing and moisturizing agent.

A paper published in 1998 (14) by researchers at Shiseido and at the UCSF Department of Dermatology entitled "Low humidity stimulates epidermal DNA synthesis and amplifies the hyperproliferative response to barrier disruption: Implications for seasonal exacerbations of inflammatory dermatoses" provides important therapeutic insights. The results confirm the experiences of many individuals with skin conditions such as atopic dermatosis and psoriasis that these conditions tend to worsen during the winter season, when humidity is much lower.

Their studies on murine skin demonstrated that seasonal changes caused by low relative humidity can be prevented either by occlusion with materials such as petrolatum, or application of a 10% glycerin solution in water. Results show that increasing stratum corneum moisture content, whether by occlusion or by humectant treatment, prevents or reverses the development of epidermal hyperplasia.

INFLUENCE OF FORMULATION VARIABLES ON THE EFFICACY OF GLYCEROL

Future research certainly will provide additional understanding of glycerol's numerous benefits as a functional skin care active. I will now summarize available information related to formulation of glycerol in skin care products with the aim of optimizing performance and of enhancing cosmetic aesthetics.

Several publications offer insights on the influence of formulation variables on the efficacy of glycerol (12,13,15,17); however, much information in this domain falls within the category of industrial expertise and know-how.

A cosmetic chemist is faced with a significant formulation challenge when formulating with glycerol at levels beyond 10% because of its high viscosity and the tackiness that it can impart to formulations. Approaches to mitigate this negative frequently involve the use of specialty hydrophobic powders such as aluminum starch octenylsuccinate (15). I personally know of a specific example whereby an efficacious, prototype formulation containing 25% glycerol was made commercially viable when this starch derivative was introduced in the early 1970s. The inclusion of about 5% of the above-mentioned hydrophobic starch significantly improved application properties and sensory characteristics of the skin cream. I have also learned from a respected cosmetic industry consultant that the inclusion of branched chain esters in emulsion systems also serves to improve the application properties of formulations with high glycerin levels.

In the publication by Shapiro (12), he states that the performance of high-glycerin formulas was in part due to their unique formulations—"that is, emulsification systems which create an HLB balance that facilitates highly efficient delivery of glycerin into the stratum corneum."

A recent patent issued to Epstein (16) for an oil-in-water skin care composition employing an emulsifier such as dimethyl distearyl ammonium halide with a substantially nonionizable humectant, such as glycerin, and a weakly acidic material, such as glycolic or lactic acid, was claimed to provide superior moisturization properties. A therapeutic-type commercial skin-moisturizing lotion (17) utilizing dimethyl distearyl ammonium chloride in a vehicle with high glycerin content exhibits, in my judgment, good sensory and application properties.

The formulation, shown in Table V, for a prototype cationic lotion containing 8% glycerin is claimed by the raw material supplier (18) to have exceptional application properties, from rub-in to dry-down. This type emulsion vehicle may be suitable to hold even higher levels of glycerin, while maintaining acceptable application properties and cosmetic esthetics.

A study by Fluhr *et al.* (19) has demonstrated that glycerol is capable of enhancing the skin hydrating properties of water-in-oil emulsions. In addition, they have found that a combination of 5% glycerin and 5% urea in either w/o or o/w emulsions has hydrating

Table V
Formulation for a Prototype Cationic Lotion Containing 8% Glycerin

Part A	
Behentrimonium methosulfate (and) cetearyl alcohol	1.17
Emulsifying wax NF	1.00
Stearyl alcohol NF	0.33
PPG-2 myristyl ether propionate	1.00
Pentaerythrityl tetracaprylate/caprate	0.67
Mineral oil	1.00
Petrolatum	2.00
Dimethicone 350 cs	0.50
Part B	
Deionized water	82.33
Glycerin	8.00
Part C	
Hydrolyzed whole wheat protein	1.00
Propylene glycol (and) diazolidinyl urea (and) methylparaben (and) propylparaben	1.00
	100.00%

and protective properties on the stratum corneum functions. This combination was found to be more effective than either 10% urea and slightly more effective than 10% glycerin. It is possible that urea enhances the penetration of glycerin into deeper layers of the stratum corneum and thus improves the function of glycerin.

In a study by Sagiv *et al.* (20) entitled "The efficacy of humectants as skin moisturizers in the presence of oil," the researchers found that treatments with glycerol (1 M) in water reversed skin dryness as measured by a corneometer and mexameter (measurement of erythema). When glycerol dissolved in medium-chain triglycerides was tested, no moisturizing effect was found. This study confirms previous findings that glycerol requires an optimum concentration of water to function effectively.

CONCLUSION

As indicated above, the selection of emulsifying agents and the choice of vehicle additives have the potential to influence the functionality of glycerol. Much remains to be studied systematically in these areas. I expect that future studies with glycerol formulations will include the use of liquid crystal, polymeric, and dimethicone copolyol emulsifier systems. The inclusion of appropriate skin barrier agents, such as petrolatum and or polymeric agents, is anticipated to further augment skin hydration and the protective properties of formulations containing glycerin.

Glycerol presents a wonderful example of how recent basic scientific advances, combined with diverse bioengineering technology and sophisticated clinical testing methodologies, have enabled us to gain a new appreciation for a classical cosmetic raw material with recently discovered multiple mechanisms of action.

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