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화장품 원료 중 폴리올, 오일 농도에 따른 피부 보습과 피부 표면 거칠기의 변화

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How Skin Care Ingredient Concentrations Can Modulate the Effect of Polyols and Oils on Skin Moisturization and Skin Surface Roughness

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요 약: 이 연구의 목적은 폴리올류와 오일류 등 스킨케어 원료의 농도 변화에 따라 인체 피부의 보습력과 피부 표면의 거칠기가 어떻게 나타나는가를 살펴보는데 있다. 폴리올류와 오일류는 스킨케어 제품을 만드는 데 있어서 필수적인 원료이다. 그러나, 폴리올류와 오일류가 어느 농도 범위에서 인체 피부에서 객관적 효능 및 관능적 효능의 평가를 할 수 있는지 아직 연구되어 있지 않다. 이 연구에서는 비침습적 방법을 이용하여 화장품 회사에서 일반적으로 사용하는 여러 원료들을 이용하여 농도에 따른 효능을 비교하고자 한다. 폴리올류는 글리세롤과 부틸렌 그리콜(BG)을 1:1의 비율로 혼합하여 사용하였고, 오일류는 Pursyn 4®, CEH, PTO®을 1:1:1의 비율로 혼합하여 실험에 사용하였다. 시험에 사용한 제품은 모두 O/W 에멀젼 형태이며, 0~27%dml 폴리올류, 0~35%의 오일류의 농도로 수행하였다. 본 연구자는 인체 하박 내측에 제품을 도포한 후, 피부 수분량과 각질층의 거칠기를 측정하였다. 피부의 수분량은 피부 전기용량을 이용하여 측정하였고, 피부 표면 거칠기는 피부 각질을 채취하여 SEM을 이용하여 촬영한 후, 육안평가로 그 값을 나타내었다. 피부의 수분량은 폴리올류에 있어서 상한 상관관계를 나타내며, 농도는 20%까지 강한 상관관계를 나타내었다. 오일류에 있어서는 12%의 농도 범위까지 강한 상관관계를 나타내었다. 이런한 상관계수는 통계적으로 유의하게 각각 0.629와 0.603을 나타내었다($p<0.01$). 이에 반해 피부 표면 거칠기는 농도의존적으로 폴리올류와 강한 상관성을 갖고 오일류는 6%까지 통계적으로 유의한 상관성을 가졌다. 회귀분석을 통하여 표면 거칠기를 폴리올류와 오일류로 나타내었을 때, 2:5:1의 계수 비율로 연관성을 나타내었다($p<0.01$). 향후 시험은 폴리올류와 오일류를 제외한 다른 원료들(계면활성제, 지질, 수용성보습물질 등)과 다른 비침습적 측정 방법을 이용하여 그 관계를 조사할 계획이다.

Abstract: The aim of this study was to evaluate the influence of different skin care ingredient concentrations on the effect of polyols and oils on the human skin moisturization and skin surface roughness. Polyols and oils were essential ingredients to make a skin care formulation. But these were still not understood how much concentration(s) were tested on human skin in the aspect of efficacy and sensory. We studied to examine various concentrations of ingredient by cosmetic companies using noninvasive methods. Polyols were composed of glycerol and butylene glycol (BG) as 1:1 ratio, and oils were hydrogenated polydecene, cetyl ethylhexanoate and pentaerythrityl tetraethylhexanoate (PTO®, Stearinerie Dubois Fils Co., France) as 1:1:1 ratio. All compounds were tested 0 ~ 27% polyols and 0 ~ 35% oils in O/W emulsions. We investigated the effect of water contents and the effect of stratum corneum roughness in forearm skin after application of compounds. Water contents of the skin measured by skin capacitance and skin surface roughness measured visual scoring of skin surface biopsy through the scanning electron microscopy. Water contents of the skin were highly related to amount of polyols (to 20%) and oils (to 12%). Correlation coefficients were 0.971 and 0.985 respectively ($p<0.01$), 2 h after application. Skin surface roughness was positively correlated with polyol contents in concentration dependent manner, and depend on oils up to 6%. The ratio of coefficient was 2.5 to 1 (polyol to oils) by regression analysis. Further studies will be conducted with other ingredients such as surfactants, lipids and aqueous materials, and with other methods for noninvasive measurement.

Keywords: *water contents, skin roughness, skin surface biopsy, polyol, oil and formulation*

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1. Introduction

Cosmetic products were developed formulation of various ingredients materials. Moisturizers are expected to increase skin hydration and to modify the physical and chemical nature of the surface to one that is smooth, soft, and pliable. Smoothing of the surface can be observed immediately after application of a moisturizer as a result of the filling of spaces between partially desquamated skin flakes [1]. The primary function of the epidermis is to produce the stratum corneum (SC) that protects our body from desiccation and invasion of various kinds of external attacks. It is easy to measure the water content of the SC *in vivo* by electrical methods. Thus electrical methods were used widely to evaluate a moisturizer in cosmetic company.

Replication is actually an old method within the realm of electron microscopy. Before the introduction of the scanning electron microscope (SEM), surface analysis was routinely performed by using multiple- stage replication techniques. A general feature of these techniques was the fact that they were all destructive, in the sense that the replicated material was lost in the preparation procedure. Hence, its applicability to investigation of the skin was limited to situations where skin samples were taken by biopsy.

The cyanoacrylate strip, introduced in 1971 by Marks and Dawber as the so-called 'skin surface biopsy'[2], is an established method for examination of the horny layer by obtaining a thin sheet of stratum corneum (SC) with a rapidly polymerizing cyanoacrylate adhesive. It has been used for the assessment of disorders of cornification occurring in diseases such as psoriasis, ichthyoses and pityriasis rubra pilaris, as well as in actinic keratoses and age-induced changes [3].

As the electrical method and skin surface biopsy are non-invasive, safe and economical technique, we explored its applicability for moisturizing effects of cosmetic products as concentration of ingredients on human skin. We developed a modified method of skin surface biopsy, enabling us moisturizing effects related to surface roughness. In this paper, major ingredients of cosmetic products, polyols and oils will be demonstrated effects on skin as their concentrations by electrical capacitance method and skin surface biopsy.

2. Materials and Methods

2.1. Skin Care Formulation

The subjects were instructed to apply the test emulsions (Table 1). Polyols were composed of glycerol and butylene glycol (BG) as 1:1 ratio, and oils did hydrogenated polydecene (PureSyn 4®, ExxonMobil Chemical Co., USA), cetyl ethylhexanoate (CEH, Kokyu Alcohol Kogyo Co., Japan) and pentaerythrityl tetraethylhexanoate (PTO®, Stearinerie Dubois Fils Co., France) as 1:1:1 ratio. All compounds were tested 0 ~ 27% polyols and 0 ~ 35% oils in O/W emulsions respectively.

Table 1. Formulation of Skin Care Products

	Polyols	Oils	Lipids	Aqueous materials	Surfactants	The others
Ingredients (Trade name)	Glycerol/ Butylene glycol	Puresyn4 CEH PTO	Cetos KD/ Stearic acid/ Cholesterol/ GMS 105	Bio-HE/ SC-glucan/ Moist 24	Myrj 52/ Montanov 68/ Arlacel 60	Preservative (DM:DP:PE) Thickner (Sepigel 305)
Ingredients (INCI name)	Glycerol/ Butylene glycol	Hydrogenated polydecene/ Cetyl ethylhexanoate/ Pentaerythrityl tetraethylhexanoate	Cetyl alcohol Stearic acid Cholesterol Glyceryl stearate	Sodium hyaluronate Beta-Glucan	PEG-40 Stearate Cetearyl Alcohol and Cetearyl glucoside Sorbitan Stearate	Preservative (DM:DP:PE) Thickner (Polyacrylamide/ C13-14 Isoparaffin/ Laureth-7)
Ratio	1:1	1:1:1	1.5:1.5:0.56:1	2:2:1	1.1:1.5:0.3	0.25:0.1:0.3
Conc.	0 ~ 27 %	0 ~ 35 %	4.56%	5.00% (Water: to 100%)	2.90%	Preservatives (0.65%) Thickner (0.70%)

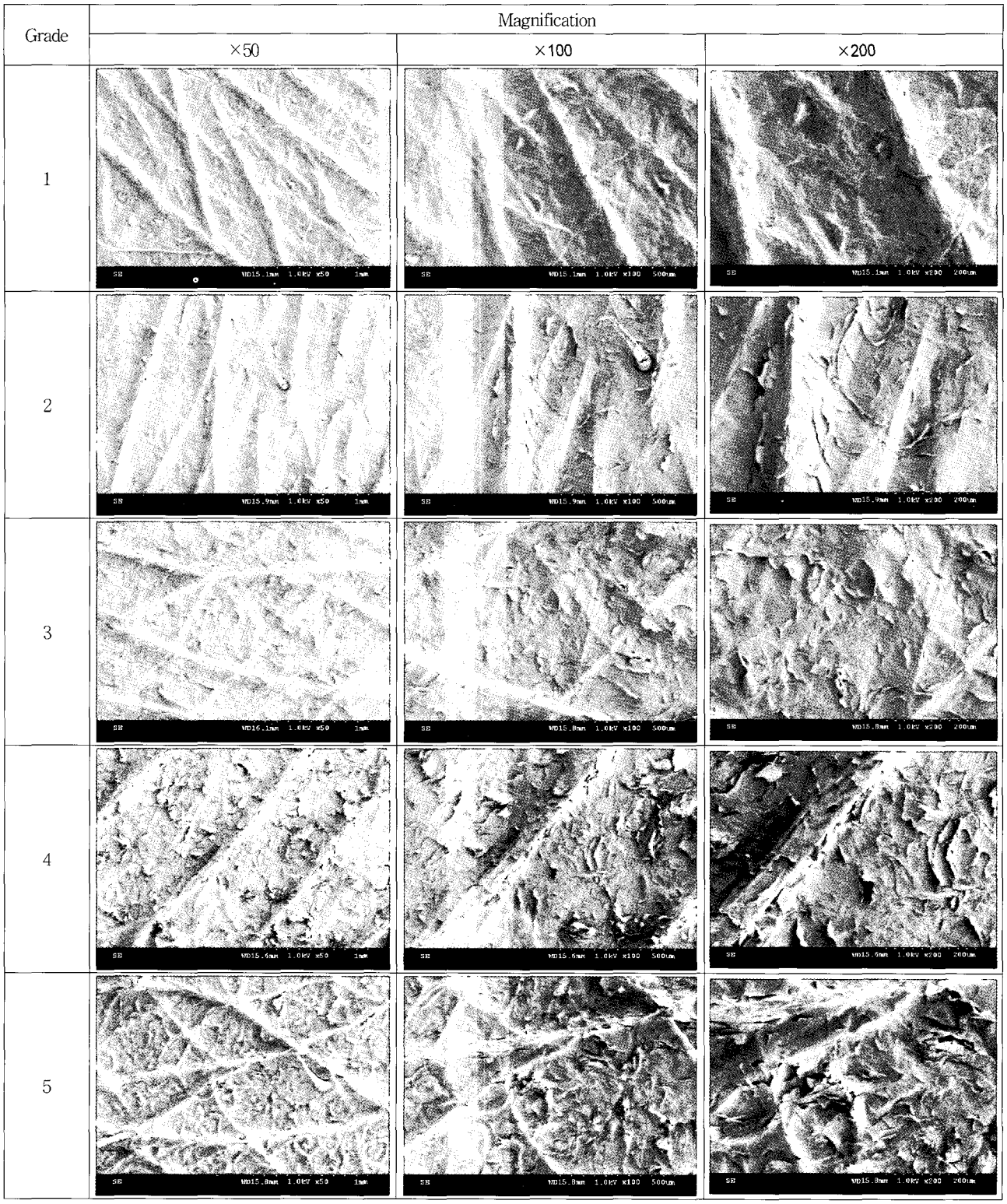


Figure 1. The grade of skin roughness by visual scoring. The basis of three magnification, ×50, ×100 and ×200, the number of mark was given points from 1 to 5.

2.2. Skin Capacitance Measurement

The moisture content in the stratum corneum was measured with a Corneometer CM825 (Courage+Khazaka Electronic GmbH, Kö ln, Germany) [4]. This device is based upon a capacitance measurement. Water increases the capacitance of the capacitor compared to a vacuum. An alteration in the amount of water in the stratum corneum, therefore, leads to a change in capacitance of the measuring capacitor. We analyzed the averages of three measurements of each site with the CM825. Water content increase rate equation as follows;

Water content increase rate (%) = (((capacitance at indicated time on application site - baseline capacitance on application site) - (capacitance at indicated time on untreated site - baseline capacitance on untreated site)) / ((capacitance at indicated time on untreated site - baseline capacitance on untreated site) + baseline capacitance on application site)) × 100%.

2.3. Skin Surface Biopsy

A droplet of cyanoacrylate adhesive (Loctite, Henkel, Ireland) was dripped from a distance of 5 cm to the centre of a lipid-free, precleaned glass slide. The glass slide was then immediately pressed to the skin surface of the central forearm, so that the adhesive spread and polymerized. After 1 min, the slide was quickly removed like a tape. To avoid external lipid contamination, investigators took care not to touch at any time the centre of the slide, to which the sample of SC adhered.

2.4. Scanning Electron Microscope (SEM)

Immediately after normal adult Korean skin adjacent to application sites were obtained at skin surface biopsy, they were cut into 5 × 5 mm pieces. Subcutaneous fatty tissue was removed. Then the specimens were processed by the osmium-DMSO-osmium method, which was developed to stereoscopically visualize intracytoplasmic organelles by removing the cytoplasmic matrix as described previously [5]. At magnification of ×50, ×100 and ×200, SEM features of skin surface were seen as a visual scoring of the skin roughness (Figure 1).

2.5. Study Protocol

2.5.1. Measurement of Physiological Change after Application of Formulated Products

The ventral side of the forearm was used as the test site. The skin surface of the test site was measured using a Corneometer and skin surface biopsy at 1 h after washing once with soap as the 0-h point of measurement. The skin surface was chronologically measured immediately after application of the test products and 2, 4 and 6 h later as Corneometer. In case of skin surface biopsy, 0, 0.15 and 6 h later.

2.5.2. Relationship Between Physiological Parameters and Ingredient Concentration of Formulation

Ventral forearm of healthy volunteers. In total, 60 Korean male or female volunteers in good health (20 ~ 35 years of age) participated in this test. Test sites were on the ventral forearm. In order to avoid environmental influences, volunteers were allowed to relax in a room maintained at a temperature of 25 ± 2℃ and a relative humidity of 40 ± 2% for 30 min after washing their forearms with soap. Then, measurements of moisture in the stratum corneum and skin surface biopsy were performed. Following these measurements, skin surface replicas were obtained from the same test sites.

2.6. Statistical Analysis

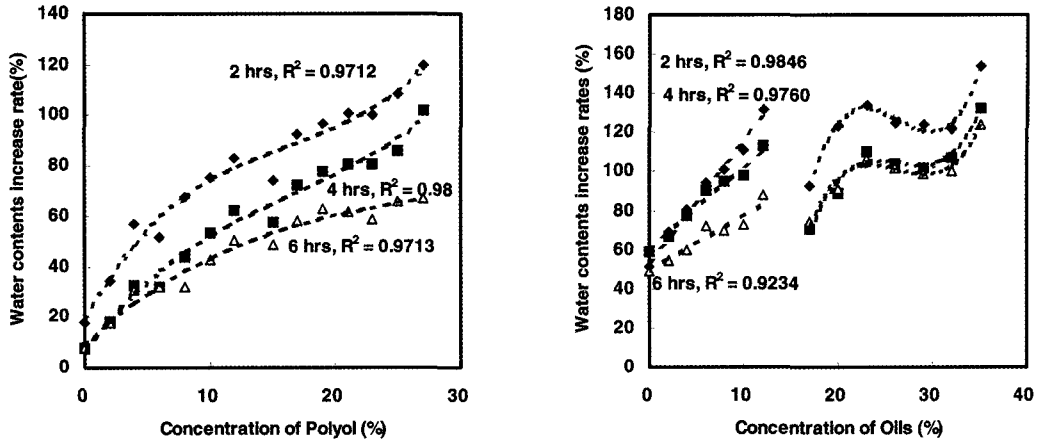
SPSS 10.0 (SPSS Institute, Chicago, IL, USA) was used for statistical analysis.

3. Results and Discussions

3.1. Effects of Water Contents Correlation with Polyols and Oils

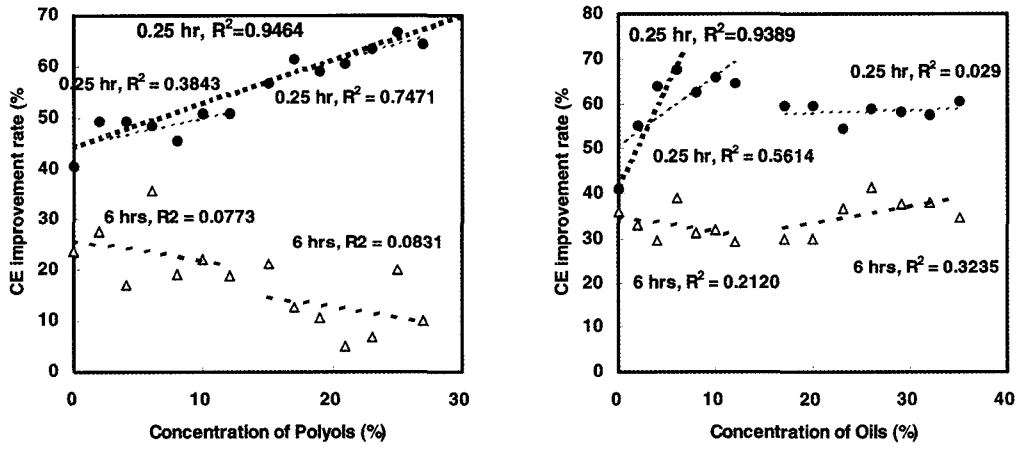
We investigated the effect of water contents and the effect of stratum corneum roughness in ventral forearm skin after application of various formulations. Water contents of skin using by capacitance, were highly related to contain polyols and oils respectively (Figure 2). Water contents increased concentration dependant of polyols and oils.

As shown Figure 2(A), correlation coefficients were 0.9712 (at 2 h), 0.9800 (at 4 h) and 0.9713 (at 6 h)



(A) (B)

Figure 2. Effects of water contents increase rate (%) as polyols and oils concentration. Each content of ingredients were separated by low and high section. (A) Concentration of polyols, (B) Conentration of oils.



(A) (B)

Figure 3. Effects of CE improvement rate (%) as polyols and oils concentration. Each content of ingredients were separated by low and high section. (A) Concentration of polyols, (B) Conentration of oils.

respectively. Increase rate of water contents were decreased as time went on. When only glycerin applied on stratum corneum as polyols, water contents increased until it was included 20% (w/v). Over 20% of glycerin, it did not increased and remained plateau graph(data not shown).

Low concentration of oils (0 ~ 12%), it was highly relation to water contents (Figure 2(B)). Correlation coefficients were 0.9864 (at 2 h), 0.9760 (at 4 h) and 0.9234 (at 6 h), respectively. But high concentration of oils (15 ~ 35%), it did not related to water contents.

3.2. Effects of Skin Roughness Correlation with Polyols and Oils

Figure 3 shows the roughness change of stratum corneum after the application of formulations on the ventral forearm. Skin roughness was improved immediately after application of products in 0.25 h. It did not effect on skin roughness at 6 h. As show to polyols, cornified envelope (CE) improvement rate was highly relation to polyols concentrations (R^2=0.9464). But it was not relation to oils concentrations (low R^2=0.5614 and high R^2=0.029 respectively). Very low concentration of oils (to 6%) was related to CE improvement rate

Table 2. Stepwise Multiple Regression Analysis of Water Contents and Skin Roughness

Parameter	Measuring time (h)	Possible equation	(P value)	Multiple correlation coefficient
Water contents Increase rate	2	= Polyols	0.001	0.907
		= Polyols + Oils	0.001	0.961
	4	= Polyols	0.001	0.911
		= Polyols + Oils	0.001	0.940
	6	= Polyols	0.001	0.858
		= Polyols + Oils	0.001	0.922
CE improvement rate	0.25	= Polyols	0.001	0.732
		= Polyols + Oils	0.001	0.939
	6	= Polyols	0.200	0.250
		= Polyols + Oils	0.001	0.759

(R^2=0.9389).

3.3. Effects of Physiological Parameters with Polyols and Oils

Due to possible complex effects of water contents and skin roughness on polyol and oil in stratum corneum, the relationship between ingredients obtained was statistically analyzed by stepwise multiple regression analysis. The results are shown in Table 2. Polyols of O/W emulsion was remarkably influenced by the water contents in the stratum corneum (multiple correlation coefficient R=0.907), and the skin roughness also had an influence. Oils were the most powerful factor for skin roughness.

4. Conclusion

(1) Water contents of the skin were highly related to contain polyols (to 20%) and oils (to 12%), respectively. Correlation coefficients were 0.629 and 0.603, respectively ($p<0.01$).

(2) Skin surface roughness was not only highly related to contain polyols depend on concentration and oils (to 6%), but also correlated the ratio of 2.5 to 1 (polyols and oils) by regression analysis.

(3) Skin surface biopsy was useful tool for skin roughness. We thought that it might be related to evaluate a sensory after using cosmetic products because it measured on 15 min. Moreover it offered a mildly-invasive, convenient collect and visual data.

(4) Further studies will be conducted with other ingredients such as surfactants, lipids and aqueous materials, and with other methods for noninvasive measurement.

References

1. S. Nicholls, C. S. King, and R. Marks, Short term effects of emollients and a bath oil on the stratum corneum, *J. Soc Cosmet. Chem.*, **29**, 617 (1978).
2. R. Marks and R. P. R. Dawber. Skin surface biopsy: an improved technique for the examination of the horny layer, *Br. J. Dermatol.*, **84**, 117 (1971).
3. C. Pierard-Franchimont and G. E. Pierard. Assessment of aging and actinic damages by cyanoacrylate skin surface strippings, *Am. J. Dermatopathol.*, **9**, 500 (1987).
4. E. Berardesca. EEMCO guidance for the assessment of stratum corneum hydration: electrical mehods, *Skin Res. Technol,* **3**, 126 (1997).
5. K. Tanaka and T. Kinose, Three-dimensional micro-anatomy of intracellular structures-special reference to Golgi complex, in Three Dimensional Micro-anatomy of Cells and Tissue Surfaces, Allen, D. J., Motta, P. M. and DiDio, L. J. A., Eds., *Elsevier North Holland, New York*, **21** (1981).