DYEING BEHAVIOUR OF WOOL FIBRES WITHOUT INTERNAL LIPIDS

M Martí, R Ramírez, L Coderch and JL Parra

Chemical and Environmental Research Institute of Barcelona, (IIQAB-CSIC).
Jordi Girona, 18-26, 08034 Barcelona (Spain)

ABSTRACT

Wool is a natural fibre with a main protein composition and with an external lipidic content widely used in cosmetics (lanoline) and an internal lipidic content in a small proportion (1.5%), which could be of added value because of its high content of ceramides. Internal wool lipids (IWL), which are rich in ceramides, cholesterol, free fatty acids and cholesteryl sulphate, have proved to be beneficial in pharmaceutical and cosmetic formulations in the treatment and care of skin and human hair.

In order to obtain IWL extracts with a large amount of ceramides, different extraction methodologies such as Soxhlet using organic solvents or supercritical fluid extraction (with CO_2 and several polarity modifiers) were optimised at laboratory and pilot plant levels. In order to determine the feasibility of extracted wool for textile purposes, the effect of lipid extraction on dyeing of wool fibres was studied.

IWL have been extracted at laboratory level and the lipidic composition was quantitatively analyzed. Extracted and non-extracted wool fibres were dyed with two acid dyes with a different hydrophilic/hydrophobic character. Dyeing behaviour and washing fastness tests were assessed.

The results obtained showed the different behaviour of extracted and non-extracted wool fibres when a hydrophilic or a hydrophobic dye was used. Maximum dye exhaustion was achieved at lower temperatures in extracted wool when a hydrophilic dye was used. However, slightly lower dye exhaustion values were obtained at all stages of the dyeing process in extracted wool when a hydrophobic dye was applied. This different dyeing behaviour may be attributed to the interaction between IWL and the dyestuff.

Therefore a lipid extraction could modify the wool dyeing strategies being able to reduce the final dyeing temperature without modifying the washing fastness of the fibres.

INTRODUCTION

Wool is a natural fibre with a main protein composition and with an external lipidic content widely used in cosmetics named lanoline and an internal lipidic content in a small proportion (1.5%) which can be of a great added value because of its high content of ceramides (1-3). Many studies have been performed in our laboratories based on the extraction, analysis and structuration of the internal lipids and isolated ceramides coming from wool (4-11). The analytical and physicochemical studies indicate a great resemblance between the internal wool lipids (IWL) and the lipids from the stratum corneum of the human skin (12-15).

IWL are rich in ceramides, cholesterol, free fatty acids and cholesteryl sulphate. The intercellular lipids of the stratum corneum play an important role in the barrier

function of the human skin by avoiding the penetration of external agents and by controlling the transepidermal water loss, which maintains the physiological skin water content (15-17). In order to obtain IWL extracts with a large amount of ceramides, different extraction methodologies such as Soxhlet with diverse organic solvent mixtures or supercritical fluid extraction with CO_2 and several polarity modifiers were optimised at laboratory and pilot plant levels (4-6, 18).

Besides the chemical analyses of wool extracts, chemical and mechanical evaluation of extracted wool was carried out. Residual grease, whiteness index, fibre diameter, fibre length, cleaning tests, alkaline solubility, bundle tenacity and drafting forces, abrasion resistance, pilling tests, and pore size were determined. Not significant changes were obtained in most of the assays between non-extracted and solvent extracted fibres. However, the superior fibre length, the lower alkaline solubility and the higher abrasion resistance on most lipidic extracted should be point out (5, 18, 19).

Additional analyses of the extracted fibres have been performed. Parameters such as yield, fibril and matrix viscoelastic behaviour, deformation work and breaking elongation have highlighted the effect of IWL on the fibre mechanical properties. The IWL extraction increased yield tenacity and decreased the elongation at break of the fibres, maintaining the feasibility of extracted wool for textile purposes (20).

A change of hidrophobicity on IWL extracted fibre could be expected, therefore, an influence on wool dyeing should be found. Wool hidrophobicity modification was also studied when wool fibres were treated with hydrophobic liposomes using Acid Green 25 and Acid Green 27 (21). The only difference between then is the length of the carbon chains. Partition coefficient measurements of them demonstrated their differences in hidrophobicity character, Acid Green 25 is more hydrophilic and the other more hydrophobic (20).

In this work, the effects of lipid extraction on wool dyeing were determined using these two different commercial acid dyes. The dyeing behaviour was assessed by comparison of dye exhaustion at different dyeing conditions and the performance of washing fastness test of extracted and non-extracted wool.

EXPERIMENTAL

Raw industrially scoured Spanish Marino (Type II) wool and wool knitted fabrics supplied by Suc. Diego Sanchez S.A. (Salamanca, Spain) were Soxhlet extracted for 4 hours with chloroform/methanol azeotrope (79:21 v/v, bath ratio 1/30), rinsed with deionised water, and dried at room temperature in the laboratory. The dyestuffs used were C.I. Acid Green 27 and C.I. Acid Green 25 (Aldrich, USA). Their chemical structures are shown in Figure 1.
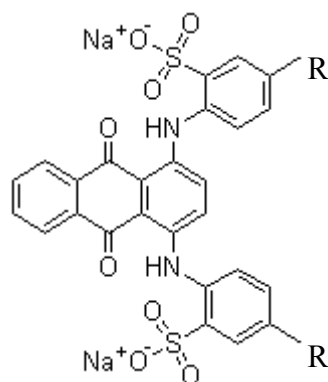
Figure 1. Molecular structure of the acid dyes used: C.I. Acid Green 27 (R = C_4H_9) and C.I. Acid Green 25 (R = CH_3).

The quantitative analysis of the lipid extraction samples was performed by thin layer chromatography coupled to an automated ionization detector (TLC-FID) Iatroscan MK-5 analyzer (Iatron, Tokyo, Japan). Samples (15-20 µg) were spotted on Silica gel S-III Chromarods using a SES (Nieder- Olm, Germany) 3202/15-01 sample spotter. A general lipid analysis was performed by eluting the rods consecutively four times using the following mobile phases: 1st and 2nd chloroform/methanol/water (57/12/0.6, v/v/v) for a distance of 2.5 cm, 3rd n-hexane/diethyl ether/formic acid (50/20/0.3, v/v/v) up to 8 cm and 4th n-hexane /benzene (35/35, v/v) up to 10 cm. After each elution, the rods were heated for 5 min at 60ºC to dry the remaining solvent. The experimental conditions were: air flow 200 mL/min, hydrogen flow 160-180 mL/min and scanning speed 2-3 mm/s. Data were processed with a Boreal version 2.5 software. These procedures were applied to the following standard compounds: palmitic acid and cholesterol from Fluka Chemicals (Buchs, Switzerland) and type II ceramide, cholesterol ester, tripalmitin and behenyl alcohol from Sigma (St. Louis, MO, USA) to determine their calibration curves for quantification of each compound. An aliquot of the different collected IWL extracts were analysed in duplicate.

Dyeing was carried out in a Redchrome (Ugolini, Italy) laboratory machine, equipped with a microprocessor Becatron AG Datex-Micro (Müllheim, Switzerland). Dyeing started at room temperature, and the temperature was raised at the rate of 1ºC/min until the maximum temperature (98ºC or 70ºC) was reached, which was maintained for 90 minutes. The wool samples were then rinsed with water and dried at room temperature. Dyebath exhaustion was determined by spectrophotometry using a Shimadzu UV-265FW spectrophotometer. Dyebath aliquots (1 ml) were periodically diluted with deionised water and added to quartz cuvettes to analyze their absorbance at maximum absorbance wavelength. All experiments were made in duplicated.

The method ISO-105/C06: 1978 (Colour Fastness to Washing) was followed to evaluate the dyed wool with or without internal lipids fastness. The dyed textile was in contact with standarized undyed multi-fibre fabric DW (ISO 105-F10) and they were agitated in a washing solution, rinsed and dried. The change in colour of the dyed textile and the staining of the undyed multi-fibre fabric were assessed using standard grey scales. This assay was made in triplicate.

RESULTS AND DISCUSSION

Raw Spanish Merino wool was soxhlet extracted with chloroform/methanol azeotrope, in order to obtain wool without internal lipids. The lipids extracted were quantitatively analysed by TLC/FID so that the main lipid families were separated and quantified.

The results of TLC-FID analysis performed following the method previously detailed in the experimental part are showed at Table I.

Table I. Lipid extract percentages: % over weight of fibres and % over total analysed.

	% over weight of fibre (owf)	% over total analysed (ota)
CHOL. ESTERS	0.03	3.22
TRIGLYCERIDS	0.02	2.42
FREE FATTY ACIDS	0.19	19.68
R-OH	0.03	3.20
STEROL	0.06	6.45
POLAR LIPIDS	0.63	65.03
TOTAL analysed lipids	**0.96**	**100.00**

It was observed that the percentage of lipids analysed was 0.96 % owf, and the main compounds are free fatty acids, sterols and polar lipids where the ceramides are included. Even though the total extracted internal lipids only account for the 0.96% of the total fibre, it is important to have in mind their fundamental role in the dyestuff penetration into fibres.

Raw wool extracted and untreated were conventionally dyed with the two acid dyes with the aim of investigate the interaction of the dye and the chemical wool structure, with and without internal wool lipids. The dyeing and diffusion properties of wool fibres are well known to be governed by all the nonkeratinous components, in which there are IWL (22-26), when these lipids were extracted the interactions with dyes could be completely changed.

Table II. Dyeing conditions.

Bath Ratio=1/30	pH= 4 (acetic/acetate buffer)
T= 25ºC-98ºC, grad=1ºC/min	T_{final}=98ºC, t=90min,
Dyestuff=1% owf of dye	
Dyes: **Cl. Acid Green 25** (levelling acid dye): hydrophilic character.	
Cl. Acid Green 27 (supermilling dye): hydrophobic character.	
Raw wool: non treated (**NT**) and extracted (**EX**)	

The raw Merino Spanish wool was dyed at 98ºC under the conventional conditions (Table II). During the temperature rise some bath aliquots were analysed. In Figure 2 it can be seen the dye exhaustion of Acid Green 25 on non treated and extracted

wool. The hydrophilic dye has high dye exhaustion reaching at 70ºC, about 99%, and the untreated wool arrives at the highest dye exhaustion at 98ºC.
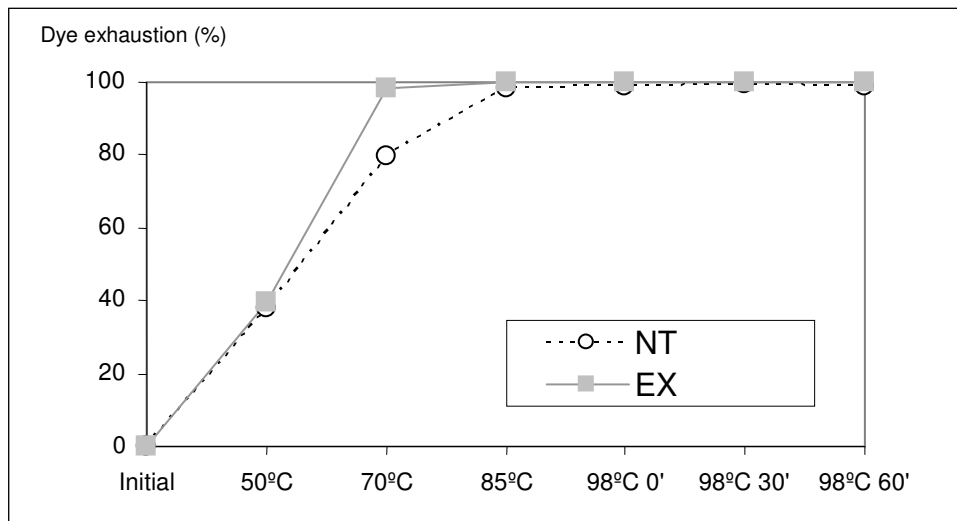
Dye exhaustion (%)

Figure 2. Acid Green 25 kinetic dyeing at 98ºC.

Acid Green 27 (Figure 3), the hydrophobic dye, has a different behaviour when the temperature increases; the extracted wool has lower dye exhaustion than the untreated wool during all the dyeing process.
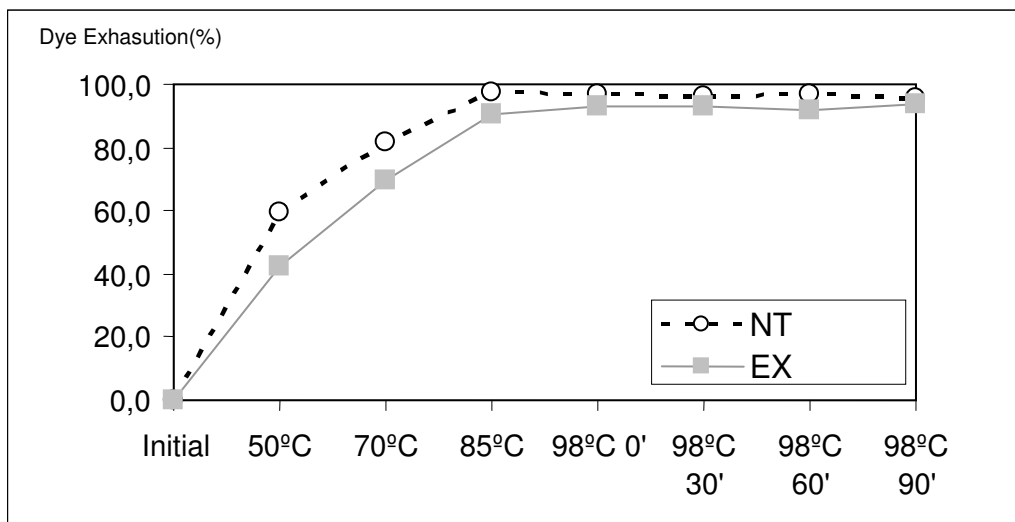
Dye Exhasution(%)

Figure 3. Acid Green 27 kinetic dyeing at 98ºC.

The absence of lipids could be the reason why the hydrophilic dye can penetrate faster into the extracted wool fibres than for untreated wool with its original composition. The interaction of this dye with short carbon chains (-CH$_3$) and its penetration in the fibres depleted of IWL are increased. The opposite happens with

the hydrophobic dye (-C_4H_9) with lower affinity to the modified wool fibre that results in a decrease dye exhaustion.

To reaffirm these results a kinetic study was performed reaching only 70ºC as a final temperature, since a maximum exhaustion was obtained for Acid Green 25 at this temperature. Therefore, two dyed process at 70ºC were performed with the same dyes (Figures 4 and 5). The dyeing conditions are the same than the previous kinetics except for the final temperature, in these cases are 70ºC.
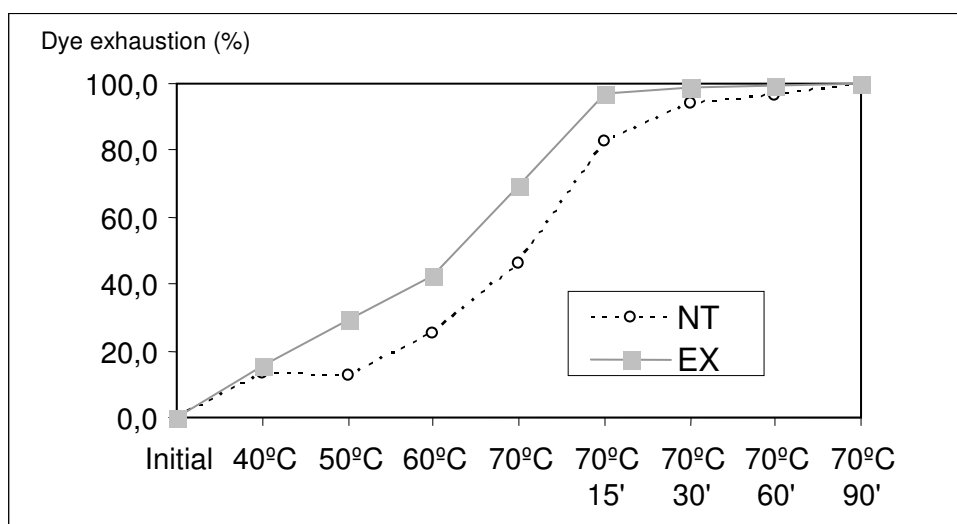

Figure 4. Acid Green 25 kinetic dyeing at 70ºC

Again, the extracted fibre is dyed faster than non treated fibre, reaching 92% of dye exhaustion after 15 minutes at 70 °C (Figure 4). These results confirmed that, as had been seen earlier, the hydrophilic dye penetrates easier when the fibre is free of lipids, which becomes more hydrophilic.
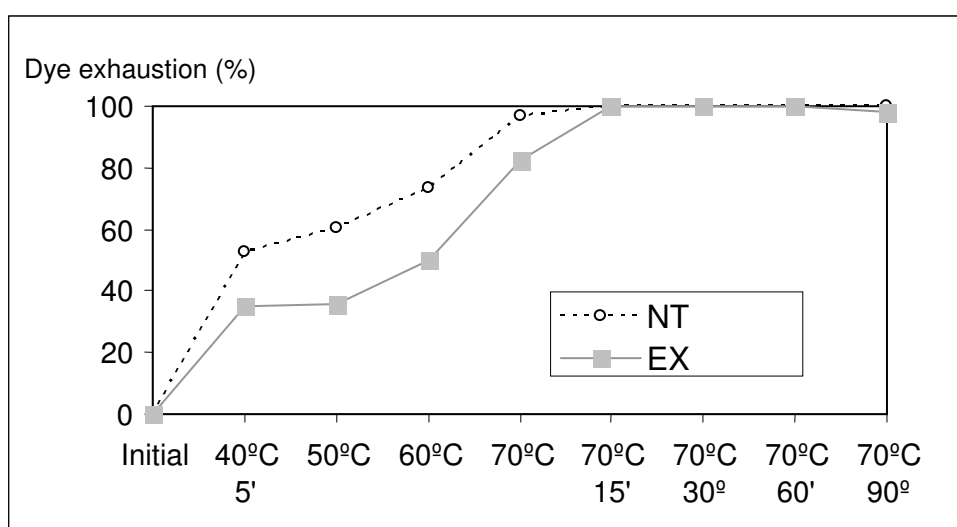

Figure 5. Acid Green 27 kinetic dyeing at 70ºC

In Figure 5, the dye behaviour is the opposite at the one previously visualized in Figure 4. The more hydrophobic is the dye, the high penetration into fibre was obtained for the non-treated sample, which maintains its lipid internal structure and has a hydrophobic character.

There have been different theories about the influence of different wool compounds in the dyeing process. Wortmann (23) and Swift (25) supported that the main pathway for dye diffusion is through the nonkeratinous components (endocuticule, intermacrofibrillar matrix and nuclear remnant zones). However, Rippon (24) and Leeder (26) lean out the intercellular cement as the pathway by which dye molecules reach cortical cells. The results obtained supported the intercellular cement as main dye pathway. The role in dyeing mechanism of internal lipids, which are only the 33% of continuous phase of wool and about 1.5% owf has to be pointed out.

With the aim to evaluate the dye fastness of wool without IWL, wool knitted fabric was Soxhlet extracted with the same conditions as raw wool fibres. Then untreated and extracted knitted fabrics were dyed using the conditions described in Table II with a final temperature of 98ºC. The method ISO-105/C06: 1978 (Colour Fastness to Washing) was followed to evaluate the dye fastness of wool fabrics with or without internal lipids. Results are given in Table III. No significant differences are observed between Acid Green 25 dyed fabrics. However, lipid free fabric dyed with Acid Green 27 shows low fastness values. This could be due to low interaction between much hydrophilic extracted fibre and the hydrophobic dye. In this case when the dyed fabric is subject to washing conditions the dye is easily release from the lipid free fibres. Besides, no significant differences are detected for the two untreated and extracted wool fabrics in the colour change.

Table III. Colour fastness to washing: Staining degree and change colour of dyed fabrics.

		Diacetate	Cotton	Polyamide	Polyester	Acrylic	Wool	Colour change
AG 25	NT	4	4-5	3-4	4-5	4-5	3-4	4-5
	EX	2-3	4-5	3	4-5	4-5	3-4	4-5
AG 27	NT	3-4	4	3-4	4	4-5	4	5
	EX	1	3-4	1-2	3-4	4-5	3-4	4-5

These results indicate that only small differences were obtained in the assessing of staining degree of hydrophobic dye, but not colour changes were obtained.

Our findings indicate a similar dyeing behaviour of wool fibres without internal lipids when a hydrophobic dye was used and a marked increase in dye exhaustion when a hydrophilic dye was applied. This strategy could be suitable for reducing the final dyeing temperature and decreasing the fibre damage without modifying the washing fastness of the fibres.

CONCLUSIONS

The results obtained showed the different dye behaviour of wool fibres with and without IWL. Two dyestuffs were used, with the only difference of the length of their chains; a shorter one more hydrophilic (Acid Green 25) and a longer one more

hydrophobic (Acid Green 27). Maximum dye exhaustion, about 98%, was achieved at 70ºC in extracted wool when a hydrophilic dye was used, with 100% of final exhaustion. However, slightly lower dye exhaustion values (93% vs. 96%) were obtained at all stages over 85ºC of the dyeing process in extracted wool when a hydrophobic dye was applied. These different dyeing behaviours may be attributed to the interaction between IWL and the dyestuff.

It may be deduced that depletion of the hydrophobic internal lipid structure from wool leads to a more hydrophilic pathway. Therefore hydrophilic dye easily penetrates into the extracted fibre, in an opposite way than the hydrophobic one. These results support the theory in which the CMC is the main pathway for dyes being the IWL fundamental in this process.

No important differences of washing fastness are observed in the dyeing with Acid Green 25, although in the dyeing with Acid Green 27 the fabric without lipids shows a slight decrease on fastness values.

Therefore, the internal lipid extraction of wool fibre has been proved to modify the dye process. On the one hand the dye exhaustion kinetics is slightly retained for hydrophobic dyes and on the other hand higher dye exhaustion is obtained at lower temperatures for hydrophilic dyes allowing reduce the final dyeing temperature to 70ºC.

Internal wool lipid extraction do not only changes the behaviour of the dyeing process for different purposes but also gives up high added value sub-product from wool fibres.

REFERENCES

1. Méndez S., Barba C., Roddick-Lanzilotta A., Kelly R., Parra JL, Coderch L., Application of internal wool lipids to hair. *Skin Res. and Techn.* (2008), (in press).

2. de Pera M., Coderch L., Fonollosa J., de la Maza A., Parra JL., Effect of internal wool lipid liposomes on skin repair. *Skin Pharmacol Appl. Skin Physiol*, **13**, (2000), 188-195.

3. Coderch L., de Pera M., Fonollosa J., de la Maza A., Parra JL. Efficacy of stratum corneum lipid supplementation on human skin. *Contact Dermatitis*, **47,** (2002), 139-146.

4. Ramírez R., Garay I., Alvarez J., Martí M., Parra JL., Coderch L. Supercritical fluid extraction to obtain ceramides from wool fibres. *Sep. Purif. Technol*, (2008) (in press).

5. Ramírez R., Martí M., Manich A.M., Parra J.L. and Coderch L.; Ceramides extracted from wool: pilot plant solvent extraction. *Textile Res. J.* (2008), (in press).

6. Coderch L., Fonollosa J., Martí M, Garde F., de la Maza A. and Parra J.L., Extraction and analysis of ceramides from internal wool lipids. *J. Am. Oil Chem. Soc.* **79**, (2002), 1215-1220.

7. Coderch L., Soriano C., de la Maza A., Erra P. and Parra J.L., Chromatographic Characterization of Internal Polar Lipids from Wool. *J. Am. Oil Chem. Soc.* **72,** (1995), 715-720.

8. Fonollosa J., Martí M., de la Maza A., Parra J.L. and Coderch L., TLC-FID Analisis of the Ceramide Content, of Internal Wool Lipids. *J. Planar Chromatogr.* **13,** (2000), 119-122.

9. Coderch L., de la Maza A., Pinazo A. and Parra J.L., Physicochemical Characteristics of Liposomes Formed with Internal Wool Lipids. *J. Am. Oil Chem. Soc.* **73,** (1996), 1713-1718.

10. Méndez S., Martí M., Barba C., Parra J.L., and Coderch L., Thermotropic behaviour of ceramides and their isolation from wool, *Langmuir,* **23**, (2007), 1359-1364.

11. Fonollosa J., Campos L., Martí M., de la Maza A., Parra J.L., and Coderch L., X-ray diffraction analysis of internal wool lipids, *Chemistry and Physics of Lipids*, **130**, (2004), 159-166.

12. Coderch L., Bondia I., Fonollosa J., Méndez S., and Parra J.L.,Ceramides from Wool: Analysis and structure., *IFSCC Magazine*, **6(2),** (2003).

13. Schaefer H., and Redelmeier T.E., Skin barrier: Principles in Percutaneous Penetration, Karger, Basel, Switzerland, (1996), 55-58.

14. Schürer NY, Plewig G, Elias PM, Stratum Corneum Lipid Function, *Dermatologica*, **183**, (1991), 77-94.

15. Kerscher M., Korting H.C., Scharfer-Korting M., Skin ceramides: structure and function, *Eur J Dermatol,* **1**, (1991), 39-43.

16. Elias P.M., Lipids and the epidermal permeability barrier, *Arch. Dermatol. Res.,* **270**, (1981), 95-117.

17. Petersen R.D., Deramides: key components for skin protection, *Cosmet. Toiletries*, **107**, (1992), 45-49.

18. Ramírez R., Martí M., Garay I., Naik A., Manich A.M., Parra J.L., Coderch L., Isolation of ceramides from wool by supercritical extraction process, 21th IFATCC Congress, (2008), Barcelona

19. Martí M., Manich A.M.; Oller P.; Coderch L.; Parra J.L. Proc. 11th Int. Wool Res. Conf., Leeds. 2005

20. Martí M.; Manich A.M.; Ussman M.H.; Bondia I.; Parra J.L.; Coderch L. *J. Appl. Poly. Sci*. **92, (**2004), 3252.

21. Martí M., Barsukov L.I., Fonollosa J., Parra J.L., Sukhanov S.V., and Coderch L., Physicochemical aspects of the liposome-wool interaction in wool dyeing, *Langmuir*, **20(8),** (2004), 3068-3073.

22. Leeder J.D. The Cell Membrane Complex and its Influence on the Properties of the Wool Fiber *Wool Sci. Rev.* **63,** (1986), 3-35.

23. Wortmann F.J., Wortmann G., and Zahn H., Pathways for Dye Diffusion in Wool Fibers, *Textile Res. J.* **67(10)**, (1997), 720-724.

24. Rippon J.A., Comments on "Pathways for Dye Diffusion in Wool Fibers", *Textile Res. J.,* **69(4),** (1999), 307-308.

25. Swift J.A., Pathways for Aqueous Diffusion in Keratin Fibres, *Textile Res. J.,* **69(2),** (1999), 152.

26. Leeder J.D., Comments on "Pathways for Aqueous Diffusion in Keratin Fibres", *Textile Res. J.,* **69(3),** (1999), 229.