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Sunlight-induced modifications in bleached, permed, or dyed human hair

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Synopsis

The influence of sunlight on cosmetically pretreated human hair was systematically investigated. Thus, bleached, permed, and dyed hairs were irradiated for four weeks with simulated sunlight, which was split into the specific ranges UV-B, UV-A, visible light (VIS), and IR. Subsequent color measurements, strength tests, and cholesterol determinations of untreated and irradiated samples showed characteristic degradation patterns in the melanin, protein, and lipid components of human hair. Comparison of the results with irradiated, untreated brown hair point to a synergistic effect between cosmetic treatments and sunlight. In particular, chemical bleaching increases a photochemically initiated brightening (VIS), loss in strength (UV-A), and degradation of cholesterol (VIS).

INTRODUCTION

The influence of sunlight on untreated human hair was extensively analyzed by examination of the protein, melanin, and lipid components as well as of the morphological areas from irradiated hair (1–3). These studies showed that the physical and chemical modifications of hair resulted in characteristic patterns of damage correlating with the pigmentation of the hair and the individual ranges of sunlight. UV-A and the visible part of sunlight (VIS) damage hair significantly; however, hair properties are also influenced to a minor extent by UV-B and IR irradiation. Black hair is largely protected from the damaging effects of the irradiation by the pigment eumelanin. In contrast, blonde hair is detectably photochemically damaged due to low pigment content or pigmentation with pheomelanin.

Some papers on the effect of sunlight on cosmetically pretreated hair, such as that which has been permanent waved, chemically bleached, or undergone oxidative dyeing, indicate a synergistic effect between pretreatment and irradiation (4,5). Thus, irradiation doses that do not cause visible modifications on natural black, blonde, or red hair lead to a clear photobleaching of dyed hair regardless of the hair color, mainly caused by the visible part of sunlight (5).

According to Tatsuda *et al.* (4), chemically bleached hair is photochemically faded to a larger extent than natural black hair. In addition, UV and VIS rays reduce the wet bundle tenacity of chemically bleached hair significantly in comparison to that of natural hair samples.

The present paper will systematically check these initial findings on synergistic damage of human hair by cosmetic pretreatment and sunlight. Thus, brown human hair was cosmetically pretreated using permanent waving, chemical bleaching, or oxidative red dyeing, and subsequently irradiated with simulated sunlight. The latter was split in a special irradiation apparatus into UV-B, UV-A, VIS, and IR so as to determine the extent of modification of the respective ranges of wavelength (1). Color and tensile strength determinations as well as quantitative determination of internal lipids (IL) using cholesterol as an example allow us to make statements about photochemical modifications of the three main components of human hair: melanin, proteins, and lipids. The final discussion takes patterns of damage as a function of the irradiation range into consideration so as to be able to develop specific measurements for sun protection of cosmetically pretreated hair.

MATERIALS AND METHODS

HAIR SAMPLES

Untreated brown hair was obtained from Herzig Co. as 25-cm-long tresses of European origin.

COSMETIC TREATMENT OF HAIR

Hair tresses were cosmetically pretreated using products from The Schwarzkopf Company. For the permanent wave treatment, tresses were reduced by ammonium thioglycolate (Style Wave X® from CLYNOL) and subsequently reoxidized for 10 min with 3% H_2O_2 (Natural Styling Stabilifix®). Chemical bleaching was achieved using a 40-min treatment with one part Igora Brilliantblond® containing 55% persulfates and two parts 6% H_2O_2 (Igora Oxigenta Lotion®). Another part of the hair sample was oxidatively dyed red for 30 min using p-toluylenediamine (one part Igora Royal Nuance R2®) and 6% H_2O_2 (one part Igora Oxigenta Lotion®). In order to obtain identical starting conditions for the hair surface, untreated, permed, bleached, and dyed hair tresses were immersed for 30 min in 1% citric acid, as this treatment is obligatorily used during bleaching.

IRRADIATION OF HAIR

The hair tresses were irradiated for a period of four weeks (672 h) in individual compartments with UV-B, UV-A, visible light, IR, or global radiation at RH > 70%. The description of the special constructed radiation chambers was given in the first part of these publications concerning the irradiation of hair (1). The applied wavelength ranges and intensities were: UV-B, 280–350 nm, 2.5 W/m^2; UV-A, 320–400 nm, 48 W/m^2; visible light, 370–780 nm, 463 W/m^2; IR, 750–2800 nm, 440 W/m^2; global light, 280–1100 nm, 1037 W/m^2. In each case a tress of approximately 2.2 cm (1.5 g) of hair was used. The tress was turned over daily to assure uniform exposure to irradiation.

COLOR MEASUREMENT

The hair color was determined in Datacolor® 3890 equipment using the CIELAB-system.

TENSILE STRENGTH TESTS

The breaking tenacity and breaking elongation were measured ten times on ten individually irradiated hairs in an Instron 1122® apparatus. The test was carried out wet, in distilled water, using a gauge length of 10 mm, a test speed of 10 mm/min, and a preload of 10 N.

LIPID DETERMINATION

The extraction of surface lipids and internal lipids (IL), thin-layer chromatographic separation, and quantitative determination of cholesterol were carried out as described earlier (3)

RESULTS AND DISCUSSION

COLOR CHANGES

For the assessment of color changes induced by irradiation of cosmetically treated hair, changes in brightness (ΔL^*) and the color coordinates on the red green axis (Δa^*) and the blue yellow axis (Δb^*) were determined after two and four weeks of irradiation according to the CIELAB system. These results are compared in Table I. A difference of >1.5 units is significant.

UV-B and IR irradiation did not cause a significant color change, whereas UV-A and VIS showed a considerable influence on the hair samples. Therefore, their resulting brightness and yellow values are represented graphically as a function of irradiation time and are discussed below. Brightening and color changes caused by sunlight occur linearly both in untreated and cosmetically treated hair with the exception of chemically bleached samples (see below).

UV-A irradiated untreated and permed hair shows after four weeks of irradiation no significant change in brightness; hair dyed red increases in brightness after this period of time by 4.5 units and bleached hair by 9 units (Figure 1).

VIS irradiated hair shows a considerably higher extent of bleaching than that irradiated with UV-A (Figure 2). Already after two weeks a significant brightening is visible both in cosmetically pretreated and untreated hair, which is further increased by another two weeks of irradiation. Chemically bleached hair brightens after four weeks of irradiation with visible light by 25.8 units, dyed hair by 10.8 units, permed hair by 6.8 units, and untreated hair by 3.9 units.

Untreated and cosmetically treated hair becomes significantly more yellow after four weeks of irradiation with UV-A (Δb^* is positive in Figure 3). Chemically bleached ($\Delta b^* = 5.7$) and dyed samples ($\Delta b^* = 5.9$) become considerably more yellow during this period of time than untreated ($\Delta b^* = 1.8$) or permed hairs ($\Delta b^* = 2.2$).

Table I

Change of Color Values on the Brightness (ΔL), Red Green (Δa), and Blue Yellow (Δb) Axes of Untreated and Cosmetically Treated Human Hair After Irradiation With Individual Parts of Sunlight for Four Weeks

		Irradiation time					
		2 Weeks			4 Weeks		
Treatment	Range of irradiation	ΔL	Δa	Δb	ΔL	Δa	Δb
Untreated	UV-B	0.3	0.3	0.2	0.6	0.5	0.5
Permed	UV-B	0.4	0.2	0.4	0	0.3	0.4
Bleached	UV-B	0.7	0.2	0.4	1.0	0.3	0.9
Dyed	UV-B	0.5	0.4	0.7	0.3	0.7	1.3
Untreated	UV-A	0.5	0.6	0.8	1.3	1.3	1.8
Permed	UV-A	0.6	0.8	1.1	1.0	1.5	2.2
Bleached	UV-A	4.0	0.6	3.4	8.2	0.7	5.7
Dyed	UV-A	2.0	1.6	2.8	4.4	2.8	5.9
Untreated	VIS	1.4	1.4	2.0	3.9	2.8	4.5
Permed	VIS	2.5	2.1	3.2	6.8	3.9	7.6
Bleached	VIS	15.6	1.2	5.7	25.8	3.8	6.1
Dyed	VIS	5.0	2.5	6.4	10.8	4.1	12.4
Untreated	IR	0.2	0.2	0.2	0.1	0.2	0.3
Permed	IR	0.6	0.3	0.2	0.5	0.4	0.5
Bleached	IR	0.9	0.2	0.1	1.4	0.2	0.1
Dyed	IR	0.5	0.3	0.6	0.8	0.5	1.1

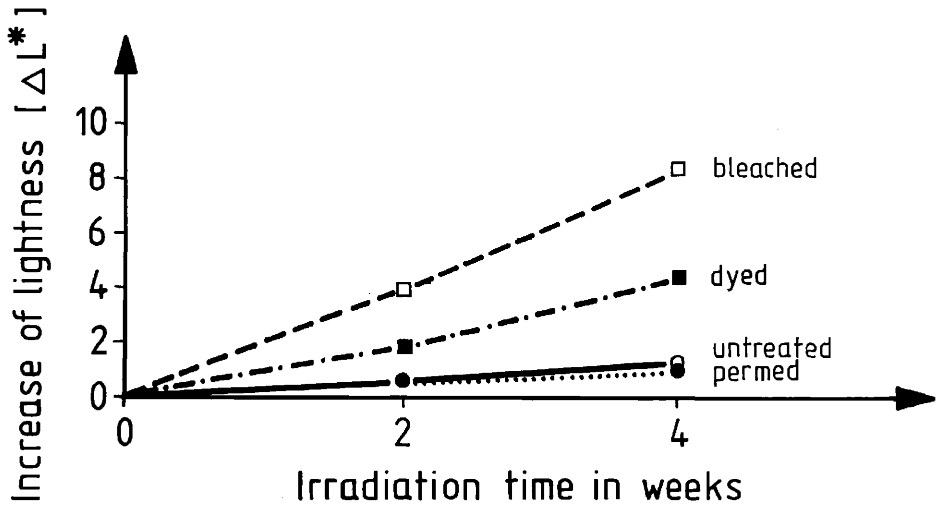

Figure 1. Increase in lightness of untreated, permed, dyed, and bleached human hair after irradiation with UV-A.

Treatment for four weeks with visible light (Figure 4) leads to stronger yellowing than with UV-A. Untreated, permed, and bleached hairs show values for Δb* of 4.5–7.6 units, and dyed hair becomes more yellow by 12.4 units.

VIS caused a visible change on the red green axis after irradiation for four weeks (Table

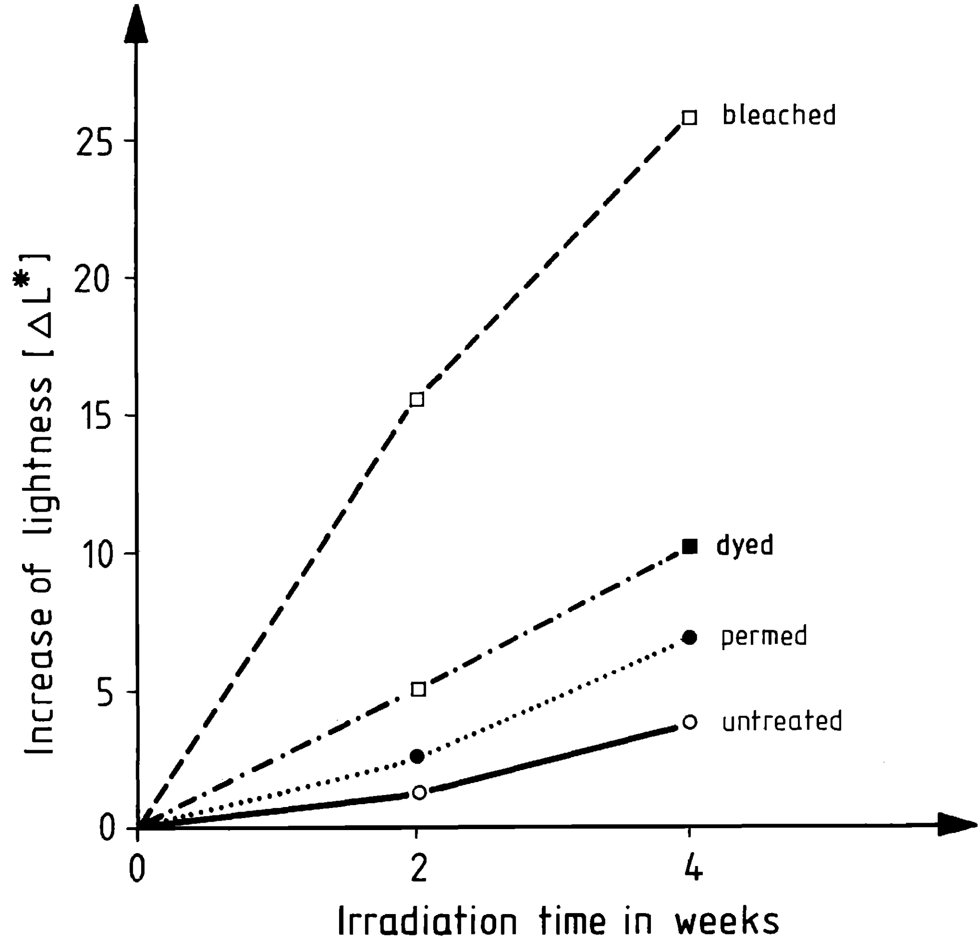

Figure 2. Increase in lightness of untreated, permed, dyed, and bleached human hair after irradiation with VIS.

I, Δa). Untreated hair becomes significantly more green (Δa* = 2.8). Cosmetically pretreated hair becomes slightly more green than untreated hair (Δa* bleached = 3.8 units; permed = 3.9 units; dyed = 4.1 units).

In comparison to permanent wave or dyeing, chemical bleaching promotes additional photobleaching of hair the most, which can be detected both after irradiation with UV-A and VIS. This photobleaching effect cannot be linearly increased by irradiation for four weeks, but instead it approaches asymptotically, just as the yellow value from bleached hair, a saturation value. This effect serves as a hint that the color pigments of hair (melanin) are largely degraded by the combination of chemical and photooxidative bleaching. There either remains a light yellow residual color or, in analogy to photochemically yellowed wool, a photochemically newly formed yellow product (6,7) is formed. The subjective observer notices a hair sample faded to a yellowish white strand.

Photochemical brightening of dyed hair occurs to a lesser extent than that observed for chemically bleached hair but to a larger extent than that observed for permed hair. After

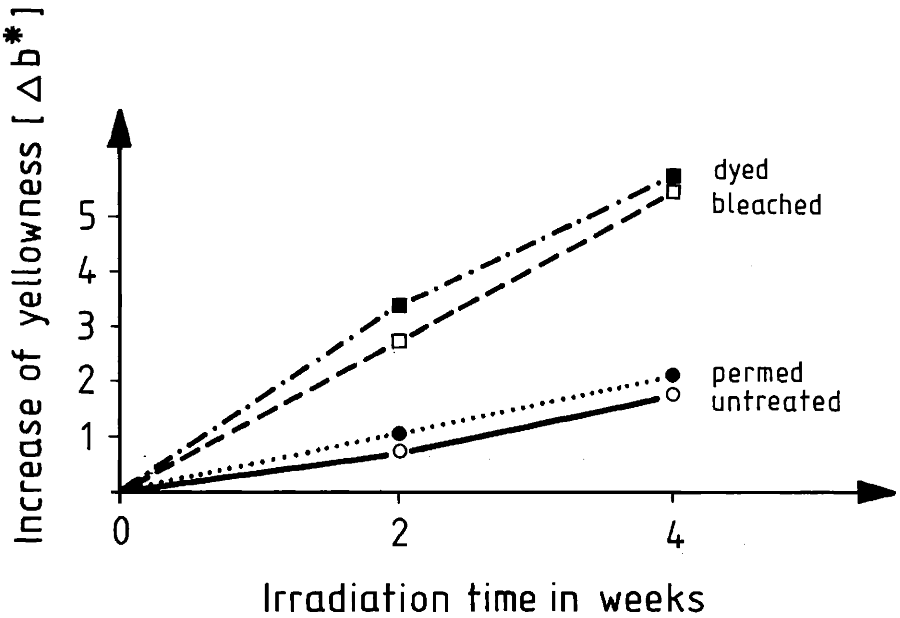

Figure 3. Shift in color on the blue yellow axis of untreated, permed, dyed, and bleached human hair after irradiation with UV-A.

irradiation for four weeks with VIS, hair dyed red is faded most heavily in comparison to chemically bleached, permed, or untreated hair. This phenomenon is accompanied by a visual assessment of a photochemically induced color change from red via orange to yellowish blonde. We assume that the red pigment introduced by the dyeing process into the hair fiber acts in addition to the natural pigment melanin as an additional photoreceptor, which is photochemically degraded parallel to the brown melanin by UV-A and especially by VIS. Thus, a more pronounced color change occurs than observed for untreated, bleached, or permed hairs.

An increase in the photochemical brightening or yellowing by a permanent-wave process is significant only after irradiation with VIS for four weeks and occurs in comparison to chemical bleaching or dyeing only to a lesser extent.

TENSILE STRENGTH TESTS

For the examination of photochemically induced changes in tensile strength, the hair bundle strength (breaking force) and the tensile stress-strain properties of the hair samples were determined. Both methods give information about the mechanical stability of the hair cortex and, to a lesser extent, of that of the cuticle (8). In the following only statistically certain reductions in tensile strength will be discussed (comparison of mean values, 95% certainty).

BREAKING FORCE

The results from the breaking force determinations are shown in Table II. A significant

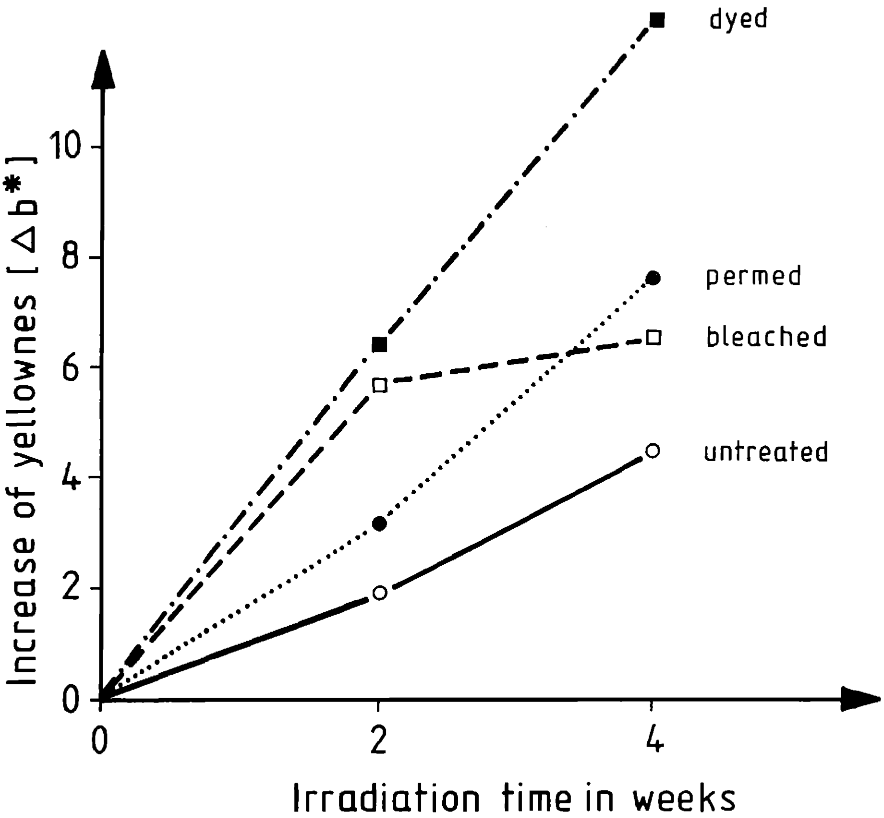

Figure 4. Shift in color on the blue yellow axis of untreated, permed, dyed, and bleached human hair after irradiation with VIS.

change in tensile strength caused by cosmetic treatments is detectable in permed hair. Since during the permanent-wave process a complete reoxidation of the reductively cleaved disulfide cross-links is not achieved, decreasing values in tensile strength support

Table II
Modification of the Breaking Tenacity of Untreated and Cosmetically Treated Human Hair After Irradiation With Individual Parts of Sunlight for Four Weeks

	Untreated		Permed		Bleached		Dyed	
	cN/tex	V	cN/tex	V	cN/tex	V	cN/tex	V
Non-irradiated	13.0	9.3	10.6†	10.5	13.3	13.5	12.8	10.1
UV-B	12.9	6.8	9.6	8.2	10.2*	10.1	11.2*	8.4
UV-A	8.6*	9.6	7.7*	7.1	5.1*	17.0	8.1*	7.2
VIS	10.1*	11.3	10.4*	13.7	9.9*	18.0	11.2*	8.6
IR	12.1	6.5	10.2	5.1	11.3*	13.9	11.7	11.9

V = coefficient of variation in %.
* = statistically certain differences between the mean values and the initial value of the non-irradiated sample, with 95% certainty.
† = statistically certain differences between the mean values and the initial value of the sample not cosmetically treated, with 95% certainty.

the indications made by Robbins (9) about a correlation between tensile strength and the number of cleaved disulfide cross-links (Table II, line 1: non-irradiated, untreated = 13.0 cN, non-irradiated, permed = 10.6 cN).

Additional irradiation, especially with UV-A, leads to a loss in tensile strength in the case of untreated as well as permed, bleached, or oxidatively dyed hair. Furthermore, a minor effect of visible light on untreated and treated hair is observed (loss in tensile strength by 2.9 cN/tex). The extent of photochemically caused losses in tensile strength is highest for bleached hair; thus, it is reduced by UV-A by *ca.* 62%, and by UV-B and VIS by *ca.* 25% in comparison to untreated hair. Regarding the influence of dyeing or permanent waving on photooxidative reduction of tensile strength, only a trend towards modification is, in comparison with untreated hair, detectable, but it cannot be measured with statistical significance.

TENSILE ELONGATION

The permanent-wave process causes a trend towards reduction of the elongation properties from 46.5% for untreated hair to 44% for treated hair (Table III, line 1: non-irradiated). The chemical bleaching process decreases the elongation of the hair fiber significantly from 46.5 to 42.4%. According to Alexander *et al.,* this effect is put down to an oxidative destruction of cystine (10). The oxidized cystine residues are more readily accessible to water molecules. An increase in water absorption follows a plasticizing effect on the fiber, which results in an increased elongation. These effects are comparable to the decrease in stiffness of swollen fibers (11).

UV-B irradiation reduces the elongation of permed hair significantly, while that of untreated, bleached or dyed hair, however, shows tendencies (Table III, line 2: UV-B). UV-A irradiation reduces the elongation properties of untreated as well as of cosmetically treated hair the most, compared with the other ranges of sunlight (Table III, line 3: UV-A).

The extent of the photochemically caused loss in elongation by VIS is somewhat less and

Table III

Modification of the Breaking Elongation of Untreated and Cosmetically Treated Human Hair After Irradiation With Individual Parts of Sunlight for Four Weeks

	Untreated		Permed		Bleached		Dyed	
	D in %	V	D in %	V	D in %	V	D in %	V
Non-irradiated	46.5	5.0	44.0	4.3	42.4†	3.2	43.9	6.3
UV-B	42.8	4.8	41.0*	10.1	41.4	10.1	40.8	10.1
UV-A	38.5*	11.7	39.0*	9.1	36.0*	7.6	38.5*	7.7
VIS	38.7*	24.8	43.6	13.6	36.6*	10.7	39.4*	9.3
IR	45.9	6.0	45.4	4.4	44.1	5.6	40.8	7.4

D = breaking elongation.

V = coefficient of variation in %.

* = statistically certain differences between the mean values and the initial value of the non-irradiated sample, with 95% certainty.

† = statistically certain differences between the mean values and the initial value of the sample not cosmetically treated, with 95% certainty.

only significant for untreated, bleached, or dyed hair. A photochemical influence of IR irradiation on the elongation properties of untreated or cosmetically treated hair is not detectable.

The major part of mechanical and consequently protein chemical damage of human hair is caused by irradiation with UV-A, followed by VIS (elongation). Both irradiation ranges cleave the S–S cross-links photooxidatively (12), which results in an additional loss in tensile strength.

Under the tested conditions, an additional effect on the irradiation-induced reduction of elongation brought about by cosmetic treatment could not be improved.

LIPID DETERMINATION

The internal lipids of hair are derived from the cell membranes of the living tissue and form *ca.* 50% of the cell membrane complex (CMC) between the keratinized cells of the cortex and the cuticle. Since this CMC plays a role in the diffusion properties of solubilized substances and is, furthermore, responsible for the cohesion of hair cells (13), the quantitative modifications of the CMC lipids were determined as a function of cosmetic treatment, and the type of irradiation was determined by quantitative determination of the cholesterol fraction. The results are shown in Table IV.

Non-irradiated, untreated hair contains *ca.* 1 mg cholesterol per gram of hair. This corresponds to 20–25% of the total lipid fraction (14). In contrast to permanent-wave treatment or dyeing, the chemical bleaching process reduces the cholesterol content of the untreated hair by 12% (Table IV, line 1: non/irradiated).

UV-B irradiation reduces the cholesterol content of permed or bleached hair only insignificantly (Table IV, line 2: UVB). The influence of UV-A (Table IV, line 3) is detectable from the reduction of the cholesterol content by *ca.* 25% in the case of untreated, permed, or bleached hair as compared to the initial concentrations. Visible light (Table IV, line 4: VIS) results in the largest photochemical degradation of cholesterol. Still, in untreated, permed, or dyed hair, 42%, 60%, and 66%, respectively, of the original cholesterol content could be detected; in chemically bleached and additionally VIS-irradiated hair, 26% of the initial cholesterol content is still detectable. This confirms the results from the most recent publications, which emphasized for the first time the photooxidative destruction of cholesterol from internal lipids in medium blonde hair by UV-A light (15) and in particular by visible light (3).

Table IV
Modification of the Cholesterol Content of Untreated and Cosmetically Treated Human Hair After Irradiation With Individual Parts of Sunlight for Four Weeks

	Amount of cholesterol in µg/g hair			
	Untreated	Permed	Bleached	Dyed
Non-irradiated	970	908	856	948
UV-B	986	836	788	916
UV-A	748	734	548	948
VIS	416	482	208	604
IR	840	884	768	780

The influence of *irradiation on permed hair* does not differ from the photochemical modifications in untreated hair. Thus, an increase in the photooxidative lipid modification by the permanent-wave process cannot be detected, which is in accordance with results from Hilterhaus-Bong (14).

Irradiation of dyed hair with VIS increases the photochemical cholesterol degradation, which is already significant in natural hair, by another 40%; contrary to what is seen in untreated hair, UV-A and UV-B do not result in a detectable photodegradation of cholesterol. This result can possibly be explained analogous to the dyeing processes in wool finishing. In that case a stabilization of the fiber occurs from the dyes introduced into the wool fiber, as these additionally cross-link the wool proteins. As a result, the fibers swell less, which in turn results, due to the reduced diffusion of water, in a lower photochemically initiated lipid oxidation.

Irradiation of chemically bleached hair results, in comparison to untreated hair and both instances of cosmetically treated hair, in the largest modification. Visible light decreases the cholesterol content by 75%, UV-A decreases it by 42%, and UV-B decreases it by 8%. Chemical bleaching accelerates the photochemical lipid degradation, which can be put down to the lower self-protection of the hair fiber by the chemically and photooxidatively degraded melanin.

SUMMARY

According to previous results (1–3), UV-A and VIS modify the morphological and chemical properties of human hair significantly, with UV-A mainly resulting in a damage of the proteins, whereas VIS mainly modifies photochemically the natural color pigments and the internal lipids. A comparison of the patterns of modification from cosmetically treated and untreated human hair after irradiation with different parts of sunlight allows statements about synergistic effects between chemical and photochemical influences.

As a result of the *permanent-wave treatment* cystine cross-links are reduced and subsequently reoxidized using 2% H_2O_2 for 10 min under partly prolonged treatments (Table V). Subsequent photooxidative processes on permed hair show only an intensification regarding the degradation of melanin by VIS. The hair brightens more in comparison to untreated samples and becomes more yellow. A trend towards an increase in an irradiation-induced degradation of proteins or lipids could, in the present investigation, only be detected with regard to loss in tensile strength.

Accordingly, permed hair shows, in contrast to bleached or dyed hair, the lowest additional damage after irradiation with sunlight and does not differ significantly from

Table V
Concentration and Duration of Contact of Human Hair with H_2O_2 During Permanent Waving, Bleaching, and Dyeing

Treatment	H_2O_2 concentration (%)	Reaction-time (min)
Permanent waving	2	10
Bleaching	4	40
Dyeing	3	30

irradiated natural hair in the extent of photochemical modifications of proteins and lipids.

Bleaching is achieved by 40-min exposure to 4% H_2O_2 (Table V), which oxidatively destroys the color pigment, melanin. As a result, hair on the whole becomes brighter. This desired effect is supported especially by irradiation with visible light and by UV-A, so that these hairs fade to a much larger extent than natural hair. However, these hairs not only become brighter, but also more yellow and more green. The protein and lipid components of human hair are already significantly damaged by the chemical bleaching process. Irradiation with UV-A and VIS leads to a further modification of both components so that considerable losses in tensile strength and decreases in the lipid content have to be accepted. In accordance with the degradation of lipids in irradiated wool, this can mean reduction in cell cohesion and plasticity of the total fiber (18). Furthermore, a loss in lipids promotes the diffusion of foreign substances along the damaged CMC into the hair fiber and thus supports further modifications of the hair (17).

Human hair is sensibilized towards photochemical modifications of all three chemical components following chemical bleaching. Melanin pigments (partly desired) and proteins and lipids (both undesirable) are particularly modified to a large extent by UV-A and visible light. Therefore, in this case a synergistic fiber damage as a result of bleaching in combination with irradiation with sunlight could be demonstrated.

Dyed hair is exposed to lower concentrations of, and shorter treatment times with, H_2O_2 than is the case for bleached hair (30 min 3% H_2O_2, c/f Table V). In addition, it is treated with a red pigment. These hairs become orange-yellow, especially after irradiation with the visible part of sunlight. It is therefore assumed that the red pigment acts in addition to the natural brown pigment in the VIS range as a photoreceptor and that it is also photochemically degraded. A protein chemical modification due to irradiation with VIS occurs to a lower extent than that observed for cosmetically untreated hairs. Furthermore, photooxidative degradation of IL both in the UV-A and the VIS range is lower. It is therefore assumed that during oxidative dyeing the color pigments attach to hair proteins in a fashion similar to that in wool dyeing, impede conformational changes, and thus stabilize the proteins because of additional cross-links (16). Therefore, H_2O_2 molecules can only diffuse to a lower extent into the hair, and consecutive photochemical reactions of the proteins and lipids are reduced (19). Thus, the present results indicate that hair can be protected by oxidative dyeing from photochemical degradation reactions, but that it is in turn subject to undesirable color changes.

MECHANISM OF PHOTODEGRADATION

In the following, several reaction mechanisms are presented that can lead to a synergistic effect between cosmetic pretreatments and irradiation of human hair.

1. Bleaching and permanent waving result in an increase in the *water retention value* as hairs show stronger swelling (20). In these cases photochemical reactions can convert water to a larger extent into highly reactive hydroxy radicals that in turn destroy in consecutive reactions the chemical components of hair (increased loss of tensile strength and lipid degradation in bleached hair). Conversely, examination of dyed hair indicates a reduced photochemical destruction because dyeing makes swelling more difficult (reduced loss in tensile strength).

2. The photochemical reactions of cosmetically modified hairs are intensified by *chemicals remaining* in the hair. In particular, H_2O_2 is taken into consideration, as (a) all examined cosmetically treated hairs had come in contact with H_2O_2 (c/f Table V), and (b) H_2O_2 can be transformed under irradiation into highly reactive hydroxy radicals (photochemical melanin degradation correlates with duration and concentration of H_2O_2 treatment).

3. *Melanin* is assigned a key role in the photochemical reactions. The extent of photochemical damage in many investigations deals with the cortex directly, dependent on pigmentation (1–4). In the present investigation, dependencies could, however, only be demonstrated between the duration of irradiation and degradation of melanin on the one hand and H_2O_2 treatment and pigment destruction on the other. Bleached hair is photochemically brightened the most, followed by dyed and permed samples.

CONCLUSIONS

On the basis of significant fading and yellowing of cosmetically treated hairs, protection against sunlight-induced (UV-A and VIS) color changes is recommended for permed and dyed hair. Chemically bleached hair needs an additional protection against photochemically caused protein and lipid modifications (UV-B, UV-A, and VIS), as these damage the structure of human hair.

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