cosmetics

MDPI

Review

Hair Lipid Structure: Effect of Surfactants

Luisa Coderch *, Cristina Alonso, M. Teresa García, Lourdes Pérez and Meritxell Martí

Institute of Advanced Chemistry of Catalonia (IQAC-CSIC), Jordi Girona, 18-26, 08034 Barcelona, Spain; cristina.alonso@iqac.csic.es (C.A.); teresa.garcia@iqac.csic.es (M.T.G.); lourdes.perez@iqac.csic.es (L.P.); meritxell.marti@iqac.csic.es (M.M.)

* Correspondence: luisa.coderch@iqac.csic.es; Tel.: +34-934006179

Abstract: Human hair fibres are mainly comprised of proteins (>90%) and lipids (1–9%), which are characterised as exogenous or endogenous, depending on whether they originate from sebaceous glands or hair matrix cells, respectively. Exogenous lipids consist of free fatty acids (FFAs), triglycerides, cholesterol (CH), wax esters, and squalene. Endogenous hair lipids comprise FFAs, CH, ceramides, glycosylceramides, cholesterol sulfate, and 18-methyleicosanoic acid. Lipids were demonstrated to be fundamental against damage and maintenance of healthy hair. Several studies have evaluated the effects of hair lipid content and have shown how hair properties were altered when lipids were removed by solvent extraction. The effect of surfactants on hair lipids is difficult to determine, as the complex structure of the cell membrane complex makes it difficult to determine where surfactants act. Shampoos and conditioners contain surfactants that remove lipids during routine cleansing of hair. However, shampooing does not completely remove all free lipids from the surface layers. The effect of surfactants on the alteration and removal of structural lipids is poorly developed, and there is no consensus on the results. Further research on the lipid composition of the hair could provide information on the penetration pathways of surfactants to improve effectiveness and limit possible damage.

Keywords: hair; lipids; surfactants

Citation: Coderch, L.; Alonso, C.; García, M.T.; Pérez, L.; Martí, M. Hair Lipid Structure: Effect of Surfactants. *Cosmetics* **2023**, *10*, 107. https://doi.org/10.3390/cosmetics10040107

Academic Editor: Enzo Berardesca

Received: 15 June 2023
Revised: 10 July 2023
Accepted: 17 July 2023
Published: 19 July 2023

1. Introduction

The human hair shaft is a filamentous structure of epidermal origin that emerges from the hair follicle. Biochemical studies of hair shaft structure have mainly focused on the composition and the function of hair proteins, whereas morphological examination of hair morphology is mainly based on diameter, shape, colour, texture and mechanical properties.

Hair lipids are crucial for protection against environmental and chemical damage; prevention of hair breakage and thinning; they serve as a barrier against moisture loss and improve the shine, elasticity, and tensile strength of the hair shaft. The lipid barrier is essential to prevent penetration of foreign materials and modification of internal moisture [1–3]. However, due to routine washing with surfactants, these hair barriers are constantly damaged and eventually lose their functions [4]. Due to the small amount and different hydrophobicity of the lipids present in the hair, it is, therefore, hard to determine the effect of surfactants on hair lipids. In addition, the complex structure of the cell membrane complex (CMC) further complicates the interpretation of where the surfactant acts [5].

Studies have investigated the effects of chemical and environmental damage on the lipid composition and properties of hair. Bleaching has been shown to deplete the outermost hydrophobic lipid monolayer and free lipids, which deteriorates the cuticle and results in a hydrophilic surface with increased friction [6–8]. Similarly, but to a lesser extent, hair treatment with dyes or permanent styling lowers lipid levels by damaging the protective cuticle layer [6,9]. Shampoos and conditioners contain surfactants that also partially

remove lipids in the routine shampooing of hair. However, there have been few studies to characterise lipid loss directly [5].

This work focuses on the study of the lipids present in the hair, their chemical composition, the structures they form and their function, in particular, their role in water diffusion. On the other hand, the state of the art on the effect of shampoos and conditioners on the lipids of the hair fibre and the possible restoration of their functionality will be reviewed.

2. Lipids of Hair—Chemical Composition and Structure

Various methods have been developed to analyse the lipid composition of hair, such as infrared or Raman spectral imaging, microscopic imaging, chemical extraction and analysis, mechanical and sensory testing, and other analytical techniques. However, biochemical studies of hair are currently limited by the difficulty of analysing the structure of single hair fibres due to their thinness and the limits of resolution of current imaging methods. Furthermore, the impossibility of separating hair layers for individual lipid content analysis limits the ability to localise a specific layer within the cross-section of the hair shaft [10].

Human hair fibres are mainly composed of proteins (>90% of the dry weight of the hair) and lipids (1–9%). They are comprised of a central medulla of weakly bound cells surrounded by tighter spindle-shaped cortical cells, with 5–10 layers of flat, overlapping, scale-like cuticle cells and a cell membrane complex (CMC) located in the intercellular spaces between the cuticle and cortical cells [1] (Figure 1).

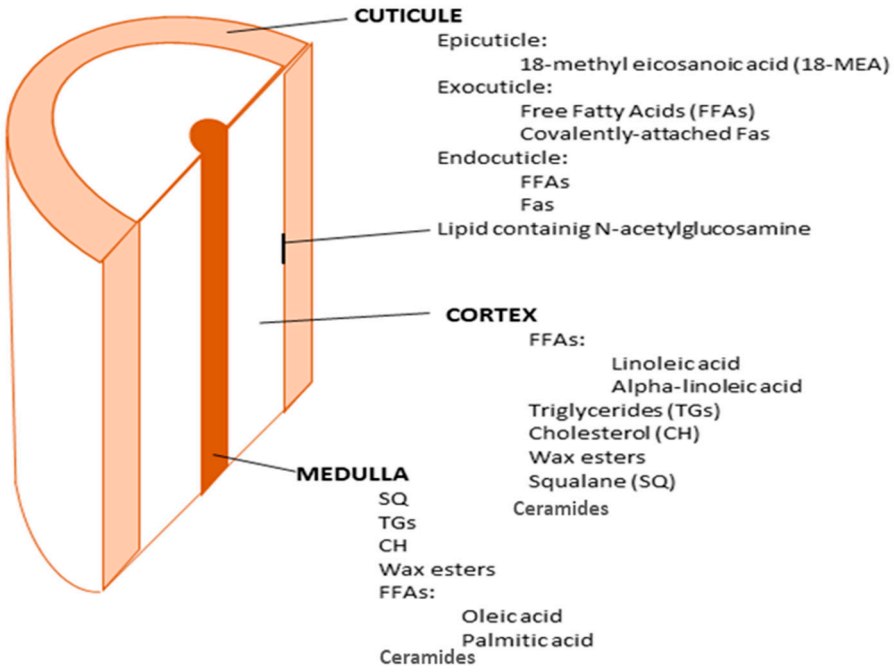

Figure 1. Hair transverse layers and lipid composition: 18-methyleicosanoic acid (18-MEA), Free Fatty Acids (FFAs), Fatty acids (Fas), Triglycerides (TG), Cholesterol (CH), Squalene (SQ).

Hair proteins are composed of a highly cross-linked amino acid, cystine (also called semicystin H-CYS) [11–13], which provides elasticity to hair fibres and contributes to their mechanical resistance to elongation, bending and twisting [1,14,15]. Hair lipids can be classified in different ways. They are defined as free or bound, endogenous or exogenous, internal or superficial, and by chemical functional group or chemical type [1,16]. Exogenous lipids include free fatty acids (FFA), triglycerides, cholesterol (CH), wax esters and squalene (SQ). Endogenous capillary lipids consist of FFA, CH, ceramides (CER), glucosylceramides, cholesterol sulphate (CS) and 18-methyleicosanoic acid (18-MEA) [17]. Among them, only 18-MEA chemically binds to the cuticle surface via a thioester bond [18]. Although lipid contents per layer vary between hair fibres, the medulla and cuticle have a relatively high lipid composition in comparison to the cortex, and cuticular lipid chains have a higher

conformational order [19–21]. The highest lipid concentrations in human hair are 4.3 mg/g FFA, 3.3 mg/g CS, 0.6 mg/g CH and 0.2 mg/g fatty alcohols [22,23]. Endogenous lipids, including sterols, FFA, CS and CER, constitute 2.5% of the total hair fibre, while exogenous lipids, such as SQ and sterol esters, account for less than 1% [17]. There are a limited number of studies investigating the lipid profile of human hair due to the difficulties associated with the low lipid content and the lack of well-established hair lipid analysis methods [10].

Lipids are located in the three main transverse layers: cuticle, cortex, and medulla (Figure 1). The cuticle is the most external layer, consisting of six to ten layers of overlapping, flattened cuticular cells that provide a protective covering for the underlying cortex [24]. The endocuticle surrounds these cells, followed by the exocuticle, A-layer and the upper epicuticle. The epicuticle comprises a hydrophobic lipid monolayer of 18-MEA, also present in the β-layer of the cell membrane complex (CMC) that keeps the hair cells attached [25–28]. The lipid content is highest at the boundary between the individual cuticle layers [19]. The lower level of the cuticle contains covalently bound fatty acids and FFA [29]. A membrane-like structure at the interface between the cuticle and the cortex is made up of sterylglucoside-like lipids containing N-acetylglucosamine [30]. The cortex comprises the major keratinised part of the hair and consists of elongated, closely packed cells parallel to the fibre axis, with a very low lipid content. However, oxidative metabolites derived from integral fatty acids, such as linoleic and alpha-linoleic acids, are non-covalently lipids and bind to melanin granules [31]. The medulla, which is the innermost portion of the terminal hair shaft, consists of a loose layer of medullary cells and empty vacuoles, which are significantly stabilised by structural lipids [32,33]. The medulla may be present, either discontinuously or continuously. The medulla contains more lipids than the rest of the hair fibre [20,34], but its composition is uncertain. Recent lipid profile results indicate that the medulla comprises squalene, fatty acids such as oleic acid, wax esters and FFA such as palmitic acid [35,36]. Another recent study confirms the high lipid concentration containing a mixture of non-esterified and esterified lipids and carboxylate soaps in various proportions [37].

Bound lipids are those that cannot be eliminated by extracting the hair with lipid solvents because they are covalently attached to hair proteins. For example, 18-MEA is bound to proteins by thioester bonds, whereas free lipids can be extracted from hair with lipid solvents because they are attached by weaker binding forces, such as van der Waals forces of attraction and sometimes hydrogen bonds or even salt bonds. Endogenous lipids are those hair lipids that result from biosynthesis in the hair matrix cells of the hair follicle, whereas those hair lipids that are usually synthesised in the sebaceous glands are sometimes referred to as exogenous from an extrinsic origin. Internal lipids are those that have either penetrated the hair or have been incorporated into the hair fibre, as opposed to surface lipids [1]. Bound lipids are those lipids of the cell membrane complex that are covalently bound to proteins, including 18-MEA bound to the epicuticle on the hair surface. 18-MEA forms part of a lipid monolayer that surrounds each cuticle cell. 18-MEA is bound to the top of each cuticle cell (and part of the scale edge) by thioester bonds [38]. In addition, 18-MEA forms the outer surface layer of the virgin hair surface, as well as the top layer of each cuticle cell. The function of 18-MEA is unclear, although it is believed that the pendant methyl group disrupts the packing of this monolayer, thus producing a disordered surface that may confer beneficial tribological properties [39]. The presence of branching alters the degree of arrangement on the surface and drastically impacts the observed frictional behaviour, inducing a liquid-like behaviour [40].

The bottom of each cuticle cell and part of each scale edge are mostly covered by straight-chain fatty acids, which are mainly palmitic, stearic, and other fatty acids, including some oleic acid. These fatty acids are linked by ester or thioester bonds to the underlying proteins. All other lipids described in the literature are believed to be free lipids, i.e., lipids that are not covalently bound to hair proteins and exist in the cuticle and cortex. On the hair surface, 18-MEA was found to be the main lipid, but there is also free lipid that can be

removed by shampooing or solvent extraction. The 18-MEA chains can then fold back on themselves, as Zahn et al. [41] suggest. Thus, as additional free lipid is incorporated into the 18-MEA layer, it allows the 18-MEA chains to be straightened to accommodate the free lipid, approach the expected length of 18-MEA, and occupy a greater percentage of the top 3–5 nm of the surface.

Lipids play a structural role in supplying hair with a cell membrane complex (CMC), which is present in both the cuticle and cortical cells. In recent years, the structural details of the CMC of both the cuticle and cortical cells, as well as the interface between the cuticle and cortex, have become better understood [42]. There are two parts of the cuticle CMC, which are usually classified as the upper and lower β-layers. The upper β-layer consists of covalently bound 18-MEA, which is believed to form a monolayer intercalated with other free fatty acids, which are assumed to be stabilised by van der Waals and electrostatic interactions. The upper β-layer is located in the upper lamina of the cuticle cell and is exposed to the external environment. It is also present at the top of each underlying cuticle cell, where it comes into contact with the lower β-layer of an overlying cell. Situated at the bottom of the cuticle cell, the lower β-layer consists of a monolayer containing free fatty acids and covalently bound fatty acids (but not 18-MEA). The lower β-layer of an overlying cell is separated from the upper β-layer of an underlying cell by the delta layer, the intercellular cement that holds the two cells apart, which is believed to be glycoprotein or globular protein (Figures 1 and 2).

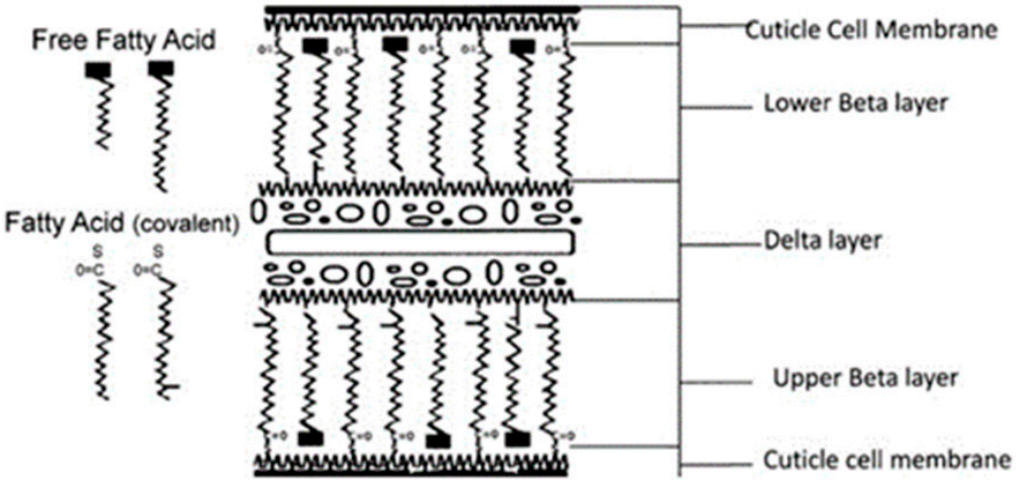

Figure 2. Schematic of the CMC (lower and upper β layers) of two overlying cuticle cells. The lower β layer corresponds to the overlying cell, whereas the upper β layer corresponds to the underlying cell. Reprinted with permission from Society of Cosmetic Chemists. Copyright 2009. Originally appeared in Reference [42].

In contrast to the upper and lower β-layers of the cuticle, which contain a mixture of covalently and non-covalently bound lipids, the CMC of cortical cells is made up of free fatty acids, cholesterol (or cholesterol sulphate) and ceramide [42]. The outer edge of each cortical cell is surrounded by a bilayer structure, the cortical CMC, which also contains a delta layer that acts as an interface with another cortical cell. Thus, two adjacent cortical cell bilayers are separated by a thin delta layer (Figures 2 and 3). The interface between the cuticle and cortical cells is a composite CMC formed on the cuticle side by a mixed monolayer of covalently and non-covalently bound fatty acids (lower β-layer) and on the cortical side by a bilayer of free fatty acids, cholesterol, and ceramide. The cuticular monolayer and the cortical bilayer are also separated by a delta layer.

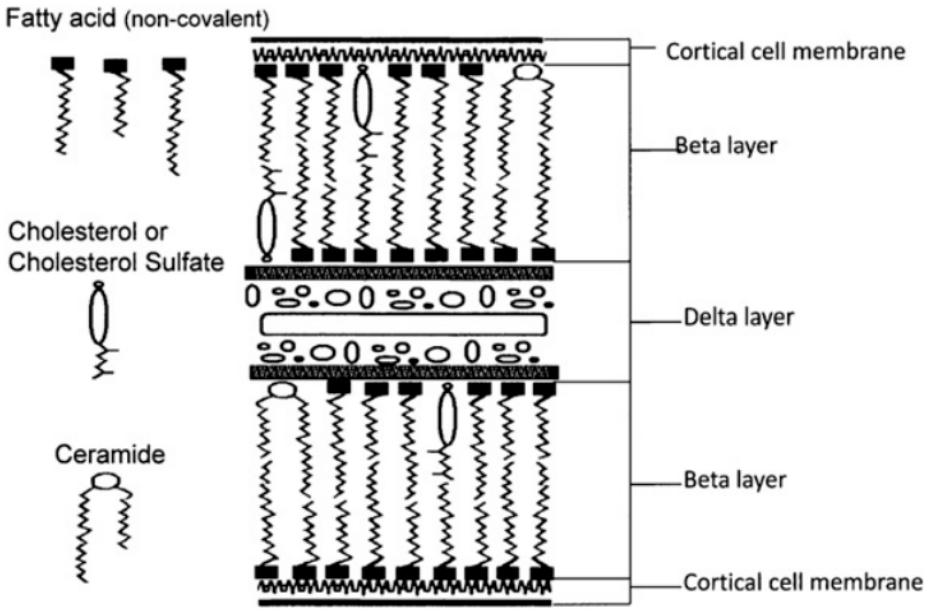

Figure 3. Schematic of the cortical CMC of two adjacent cortical cells separated by a delta layer. Reprinted with permission from Society of Cosmetic Chemists. Copyright 2009. Originally appeared in Reference [42].

3. Lipid Role in Hair Properties

Given that hair lipids are present both in the CMC and on the surface of cuticle cells, they appear to play a role in various physicochemical properties of hair fibres, such as chemical diffusion barrier, water retention property and cell cohesion [43–46]. Lipids play an important role in the functional and structural properties of hair, which are described herein.

In recent years, considerable attention has been paid by the research community to structural lipids, especially covalently bound 18-MEA [47–49]. Lipids of sebum origin were often considered less important or even a nuisance and were thought to play little or no functional role in hair. In the skin, sebum is an integral constituent that plays a protective functional role. Multiple studies have evaluated the effects of hair lipid content and its relationship to the clinical properties of hair. McMullen [2] highlighted the altered properties of hair when lipids were removed by solvent extraction and showed differences in moisture handling, interaction with cationic polymers and surfactants and impact on hairstyle hold. During the extraction procedure, both sebaceous and free structural lipids were removed from the outside and inside of the fibre (covalently bound lipids were not removed). For this reason, it is difficult to discern differences in the structural/functional contributions of sebum or free structural lipids to the measured fibre properties. There were no discernable differences between untreated virgin hair and delipidised hair in terms of rigidity, elasticity, or DSC phase behaviour. However, increased combing energy, decreased contact angle, high water uptake and higher hysteresis (more resistance to water release) were observed in delipidised hair. Ishihara et al. [50] have recently confirmed the increase of water in formic acid delipidised hair, proposing a water distribution on the β-layer.

External extraction followed by internal lipid extraction with different solvent systems without external modification of 18-MEA has been studied [17]. External lipid extraction partially decreases the hydrophobicity and induces a reduction in the water content of the fibre, probably due to a disordering of the remaining surface lipids, whereas internal lipid extraction makes the internal fibre more polar by increasing the water content. Lipid extraction from the medulla could increase the polarity inside the fibre [17]. It is important to underline that the claim regarding hair hydration is puzzling [51]. The water content of hair is overwhelmingly dictated by the relative humidity (RH) of the environment, but while consumers profess a desire for "maximum hydration", high humidity conditions that

induce this state represent the very definition of a bad hair day. Furthermore, technically, as the hair becomes more damaged, it has a greater affinity for water. Theoretically, therefore, the consumer term "dry and damaged hair" would seem contradictory [51]. Therefore, external lipid extraction would ameliorate the fibre, decreasing the water content, while internal lipid depletion would damage the fibre, increasing its moisturisation.

Kinetic evaluation of the water absorption/desorption process is a good approach to determining the structural integrity of fibres. There is a slight decrease in water diffusion in fibres extracted from external lipids, which was more marked after the extraction of internal lipids. The extraction of highly unsaturated internal lipids could be responsible for a decrease in water permeability and an increase in the breaking strength of the delipidised internal fibres.

A decrease in hair lipid content has been associated with decreased tensile strength and increased hair breakage [17,52]. Tensile properties decline from root to tip, along with levels of 18-MEA, CS, CH, CER and bound fatty acids, potentially due to grooming and environmental stress [49–52]. Hair fibre texture and shine are also affected by lipid content and removal. Hair gloss is reduced with decreasing unsaturated lipid content in the medulla due to an altered refractive index, thus decreasing both penetrating and scattered light from the hair surface [53]. The removal of surface 18-MEA decreases hydrophobicity and increases surface friction, causing the hair to dry, tangled and untidy [54].

Hair differences can be related to geo-racial origin [55]. The effect of lipids on the properties of hair of different ethnicities has been determined. African hair has the highest lipid content with 6%, Caucasian hair is composed of 3% lipids, and Asian hair has 2% lipids [56]. Moisture resistance is related to the fluidity of lipids in the cuticle. Caucasian fibres, with their highly ordered lipids, are more resistant to moisture absorption and are also the most hydrated [56,57]. Comparatively, African hair has the lowest lipid order and the highest water diffusion rate, despite the high lipid content of the cuticle [57]. Other studies have found that hair fibre permeability and moisture resistance are not affected by lipid removal [17,58]. African hair has a low initial modulus and lower deformation at breakage, which corresponds to weaker and more brittle hair [53]. The structure of African hair is influenced by the high lipid content; lipid intercalation of keratin dimers interferes with their structural arrangement and may be responsible for the characteristic texture of African hair [59]. Caucasian fibres depleted in external lipids also exhibit higher lipid order and increased breakage toughness [7,53]. Asian fibres have the highest linear mass and tensile strength [56].

Hair ageing is different depending on ethnicity [60,61]. In general, grey hair fibres, with reduced unsaturated lipid content, have a lower capacity to absorb water, which contributes to their clinical "stiffness" compared to pigmented hair fibres [59]. Reduced lipid content of the cuticle, cortex and medulla occurs with advancing age and influences the clinical properties of grey hair [62]. The reduced exogenous and endogenous lipid profile of grey hair includes lower levels of 18-MEA and reduced de novo synthesis of dihydroceramide after the age of 30 years [8,63,64]. Compared to brown hair, white hair has lower internal lipids, composed mainly of free fatty acids and ceramides, lower levels of embedded water and higher water diffusion, indicating higher permeability [65]. Grey hair is less resistant to brushing stress, and ageing accelerates the loss of the cuticle barrier of the hair, leading to thinner and potentially stiffer hair [66,67]. Changes in hair follicle lipid profiles associated with age-induced hair greying have also been determined [68].

The effects of chemical and environmental damage on the lipid composition and properties of hair have been investigated in numerous studies. Exposure to ultraviolet radiation (UVR) decreases lipid content and damages hair fibres, resulting in "dry", weak, brittle, and stiff hair. More than 90% of 18-MEA is removed from Asian hair by a cumulative dose of UVR corresponding to a 3-month summer exposure [69]. However, Asian hair is more resistant to UVR than African or Caucasian hair, essentially because it possesses the highest amount of integral hair lipids (ILL), which can provide a protective barrier against UVR-induced oxidative processes [70]. Photo-degradation of white and pigmented hair

has been evaluated by X-ray diffraction and electron microscopy. Layers of lipids present in the cuticle (4.5 nm) were found to be degraded [71]. In a recent study, LC-MS lipidomics was used to detect changes in the capillary lipidome following UV light exposure. Most of the lipids detected (vitamin A fatty acid esters, sterol esters, various ceramides, etc.) were decreased in UV-exposed hair [72]. Photodamage in hair medulla lipids has also been reported [73].

Bleaching removes the uppermost layer of 18-MEA and free lipids, deteriorating the cuticle and leading to a hydrophilic surface with increased friction [6–8]. The absence of 18-MEA and degradation of the epicuticle results in hair that feels "dry", brittle, messy and difficult to comb [6,74]. More than 80% of 18-MEA is removed in a single bleaching treatment, as the bleaching process oxidises the cysteine bonds to cysteic acid [25,69]. Similarly, hair treatment with hair dye or permanent styling decreases the levels of 18-MEA lipids, FFA and CMC on the surface, damaging the protective cuticle layer [6,9].

4. Effect of Surfactants on Hair Lipid Depletion

Hair is porous and damaged hair is extremely porous. Water absorption causes swelling of the hair shaft. Excessive or repeated chemical treatments, grooming habits, and environmental exposure cause changes in hair texture and, if extreme, can lead to breakage. Weathering is one of the main causes of progressive degeneration from the root to the tip of the hair. Normal wear and tear is due to daily grooming practices [75]. The main function of shampoos is to cleanse the hair and scalp of dirt, while conditioners soften the hair and facilitate combing.

Shampoos usually consist of between 10 and 30 ingredients, although there are products with as few as four ingredients. Products are grouped into (1) cleansing agents; (2) additives that contribute to product stability and comfort; (3) conditioning agents designed to impart softness and shine, reduce shedding, and improve ease of detangling; and (4) special care ingredients, designed to treat specific problems, such as dandruff and oily hair [76,77]. Surfactants are cleansing agents that act by weakening the physicochemical bonding forces that bind impurities and residues to the hair (Table 1). Residues are non-soluble fats (sebum) that do not dissolve in water. Surfactants in contact with water achieve the structural formation of a micelle; the surrounding water molecules attract the ionic ends of the surfactant, and the particle is then emulsified or suspended in the water. In this form, it can be rinsed off [76,77].

Table 1. Classification of the surfactants.

	Shampoo Surfactants	
Class	**Example**	**Characteristics**
Anionic	Ammonium lauryl sulfate, sodium laureth sulfate, sodium lauryl sarcosinate, sodium myreth sulfate, sodium pareth sulfate, sodium stearte, sodium lauryl sulphate, alpha-olefin sulfonate, ammonium laureth sulphate	Deep cleansing
Cationic	Trimethylalkylammonium chlorides and the chlorides or bromides of benzalkonium and alkylpyridinium ions	Hair softener
Nonionic	ethoxylated fatty alcohols, cocamide diethanolamine, coco glucosides, polysorbate 20, PEG-80 sorbitan laurate	Mild cleansing
Amphoteric	Alkyl iminopropionates (amido) betaines	Mild cleansing

Depending on the electrical charge of the polar end, surfactants are classified into four groups: anionic, cationic, amphoteric, and non-ionic. The main cleaning agents are anionic. Examples of anionic surfactants are ammonium lauryl sulphate, sodium laureth sulphate, sodium lauryl sarcosinate, sodium myreth sulphate, sodium pareth sulphate, sodium

stearte, sodium lauryl sulphate, alpha olefin sulphonate and ammonium laureth sulphate. Although very good at removing sebum and dirt, anionic surfactants are strong cleansers and can cause an increase in negative electrical charges on the surface of the hair and increase frizz and friction. To minimise damage and reduce the static electricity-generating effects caused by anionic surfactants, other surfactants called secondary surfactants such as cationic (trimethylalkylammonium chlorides and benzalkonium and alkylpyridinium chlorides or bromides), amphoteric surfactants (alkyl iminopropionates and betaines (amido)) and non-ionic surfactants (ethoxylated fatty alcohols, cocamide diethanolamine, coco glucosides, polysorbate 20, PEG-80 sorbitan laurate) are added to the formulation, [76,78]. Being positively charged, cationic surfactants rapidly bind to the negatively charged strands by the use of anionic surfactants and reduce the frizz effect. Recent works study the inevitable evolution towards more bio-based, eco-friendly ingredients, reviewing some of the new alternative hair cleaning and conditioning agents obtained from natural sources [79–81].

Conditioners are used to reduce friction, detangle hair, minimise frizz and improve combability. Conditioners act by neutralising the negative electrical charge of the hair fibre by adding positive charges and lubricating the cuticle, which reduces the hydrophilicity of the fibre. They contain antistatic and lubricating substances, which are divided into five main groups: polymers, oils, waxes, hydrolysed amino acids, and cationic molecules [78]. The most active and widely used conditioning agent is silicone [82–84]. Cationic ingredients are commonly used in many shampoo formulations with anionic surfactants to neutralise the charge and form a cationic–anionic complex, a neutral hydrophobic ingredient. Bleached and chemically treated hair has a higher affinity for conditioning ingredients because it has a low isoelectric point (higher concentration of negative sites) and is more porous than virgin hair [78,85].

Shampoos contain surfactants that remove lipids during routine skin [86] and hair washing. The ability of anionic surfactants to remove lipids from hair depends on the surfactant structure, concentration, agitation, temperature, time, and other factors [78]. In addition, surfactants such as sodium lauryl sulphate do not penetrate the fibre rapidly and cannot be expected to remove the same amount of lipids from hair at the same rate as a penetrating lipid solvent such as ethanol. Anionic surfactants are almost as effective as chloroform or ether (non-penetrating lipid solvents) in removing deposited surface lipids [78].

Dissolution or extraction of structural lipids or proteinaceous matter from hair, probably from the cell membrane complex or endocuticle, by shampooing has also been demonstrated [78]. Studies have reported that one-time shampooing can remove approximately 50% of total extractable lipids from hair [87], that 70–90% of total lipids can be removed with repeated shampooing [88], and that the frequency of shampooing had no significant effect on the rate of hair regressing, suggesting that surfactants may not directly stimulate sebaceous gland activity [87]. However, it is believed that lipids are largely removed at the surface level. The cell membrane complex at the cuticle level contains 18-methyleicosanoic acid (18-MEA) lipids covalently bound to a protein cell membrane. On the outer surface of the hair, the free lipids within the 18-MEA lipid layers are removed during shampooing [78]. The internal lipids deeper in the hair shaft are not affected to the same extent as the surface lipids. The same amount of internal lipids in dry hair versus oily hair after shampooing confirms the primary differences in the amount and composition of surface lipids. Internal lipids can move into the surface layers by the process of diffusion after repeated shampooing [1].

The effect of free lipids on the isoelectric point of wool fibres washed with detergent and extracted with various solvents was studied. Wool washed with surfactant (containing mostly free lipid) gave an isoelectric point of 3.3, while hair extracted with a more effective lipid solvent gave an isoelectric point of 4.5. Therefore, the more free lipid present in these surface layers, the lower the isoelectric point of the keratin fibres. Not all free lipid is completely removed from the surface layers by shampooing. This lipid is important for the isoelectric point, the adsorption of ingredients on human hair, and other important surface

properties of the hair [89]. Cationic polymers such as polyquaternium-55, a common conditioning agent, have a higher binding affinity to hair than cationic surfactants such as quaternium-26, but both have a lower affinity for delipidised hair [2]. This shows that the removal of lipids liberates the surface of the molecules with which the cationic polymer and the surfactant can be associated.

In short, shampooing removes lipid matter from the surface, and repeated shampooing could damage hair surface structures. These changes could be reflected in the X-ray profiles, especially in the lipid signals. The ingredients of the conditioner adsorb to the hair surface and act as a protective layer that prevents this damage. Therefore, the application of conditioner, either alone or after shampooing, could also affect the X-ray signals. In the case of shampoo and conditioner treatments, no differences were observed by X-ray diffraction before and after treatment, supporting that their effects are limited to the hair fibre surface without affecting the internal lipid composition of the cell membrane complex [90].

The external or sebaceous lipids were extracted with t-butanol and hexane to study their overall contribution to physicochemical properties [91] since this seems to be the promoting effect of the shampoo. Although not much effect was found on the structural order and mechanical properties, moisture retention decreased in the outer depleted fibres for all ethnic fibres indicating improved hair properties [51]. However, internal lipid depletion with swollen solvents such as methanol was shown to promote lipid disorder and increase moisture retention [17]. In general, chemically damaged hair absorbs more water than healthy hair [51].

On the other hand, it is also well known that daily weathering can cause loss of some internal lipids, and Masukawa [92] quantified this loss after repeated shampoo treatments with and without prior bleaching. While the 18-MEA content in the tip of virgin scalp hair exposed to daily weathering during daily life activities decreased by 35% compared to that in the root, the 18-MEA content in the tip of scalp hair fibres exposed to a single bleaching combined with daily weathering during daily life activities decreased by 80% compared to the root. In addition, 18-MEA was completely lost in the scalp hair tip exposed to repeated discolouration combined with daily weathering during daily life activities, and this decrease was the most marked among all hair lipids. Cholesterol and ceramide contents were also reduced by daily weathering by up to 50% without bleaching, while more than 80% when exposed to the repeated bleaching tested.

Recent work indicates that, during routine washing, surfactants have a tremendous effect on hair lipid loss [5]. Lipid loss due to surfactant washing depends on the relative hydrophobicity of the lipids [5]. It has been suggested that the mechanism of lipid loss is different for different types of lipids, separated into two groups. Highly hydrophobic lipids, such as SQ and WE, are removed by penetration of the shampoo surfactant into the hair shaft, whereas less hydrophobic lipids, such as FFA and CH, are lost by surfactant coating on the hair surface [5,93]. This was concluded by the fact that highly hydrophobic lipids such as SQ and WE were blocked by internal fibre modification, and less hydrophobic lipids such as FFAs and CH were more affected by surface modification (Figure 4).

Considering the effect of cosmetic treatments and daily weathering on lipid removal, Marsh [94] described a shampoo formulation (anionic surfactant SLE1S and cetyl and stearyl alcohols) containing a stable ordered gel network structure that delivers fatty alcohols into the hair. Fatty alcohols combined with cationic surfactants are also common ingredients in the formulation of lamellar phase personal care liquids [95]. It is proposed that the partitioning of the fatty alcohols occurs in the lipid-rich regions of the hair, i.e., the cell membrane complex and the medulla. They have similar volume and polarity parameters to the hair's internal saturated fatty acids, palmitic and stearic, which account for ≈25% of hair lipids [1]. These actives could replenish lost internal lipids and restore hair properties, in particular hair breakage.

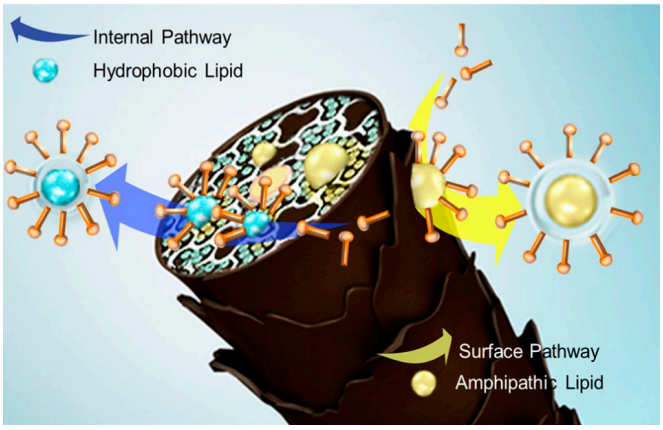

Figure 4. Schematic diagram depicting the pathways of lipid loss by surfactant [5].

5. Conclusions

Hair lipids are characterised as exogenous or endogenous, depending on whether they are derived from sebaceous glands or hair matrix cells, respectively [16]. Exogenous lipids consist of free fatty acids (FFA), triglycerides, cholesterol (CH), wax esters, and squalene (SQ). Endogenous capillary lipids include FFA, CH, ceramides (CER), glucosylceramides, cholesterol sulphate (CS), and 18-methyleicosanoic acid (18-MEA) [17]. Among them, only 18-MEA is chemically bound to the cuticle surface by a thioester bond [18]. Although the lipid content per layer varies between hair fibres, the medulla and cuticle have a relatively high lipid composition compared to the cortex, and cuticular lipid chains have a higher conformational order [19–21].

Lipids have been shown to be essential against damage and for the maintenance of healthy hair. Multiple studies have evaluated the effects of hair lipid content and highlighted how hair properties were altered when lipids were removed by solvent extraction. Lipid removal decreases the tensile strength, shine and fineness of hair while increasing permeability and desorption [23,56–58]. The lipid barrier is essential to prevent penetration of foreign matter and internal moisture modification [1–3]. Due to routine washing with surfactants, these skin barriers are constantly damaged and eventually lose their functions [4].

Some studies have investigated the effects of chemical and environmental damage on the lipid composition and properties of hair. Shampoos contain surfactants that also remove lipids in the routine washing of the hair. The ability of anionic surfactants to remove lipids from hair depends on surfactant structure, concentration, agitation, temperature, time, and other factors [78]. However, few studies have been conducted to directly recognise lipid loss. Recent work indicates that, during routine washing, surfactants have a tremendous effect on lipid loss that correlates with the relative hydrophobicity and water solubility of the lipids [5]. In contrast, lipid-based hair care products, such as conditioners, oils, serums, and masks containing natural plant oils, fats, waxes, or phospholipids, can restore hair lipids lost by damaging processes and improve hair surface texture and shine [96].

At present, the study of the lipid fraction of hair fibre has a long way to go. The impossibility of separating the hair layers to analyse the lipid content individually limits the ability to localise a specific layer within the cross-section of the hair shaft by chemical extraction methods. Furthermore, their particular role in the physico-chemical properties of the fibre is not clearly defined. Last but not least, the effect of surfactants on the modification and removal of structural lipids is poorly developed, and there is no consensus on the results. Further research on the lipid composition of hair could also provide information on the penetration pathways of hair care products, in particular surfactants, to enhance their efficacy and limit potential damage.

Author Contributions: Conceptualization, L.C.; investigation, all authors; writing-original draft preparation, L.C. and M.M.; writing-review and editing, L.C., C.A. and M.M.; supervision, M.M. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The authors acknowledge the Service of Dermocosmetic Assessment (DC-IQAC-CSIC) for its collaboration and technical support.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Robbins, C.R. Chapter 2. Chemical Composition of Different Hair Types. In *Chemical and Physical Behavior of Human Hair*, 5th ed.; Springer: Berlin/Heidelberg, Germany, 2012; pp. 105–166.
2. McMullen, R.; Laura, D.; Chen, S.; Koelmel, D.; Gillece, T. Determination of physiochemical properties of delipidized hair. *J. Cosmet. Sci.* **2013**, *64*, 355–370. [PubMed]
3. Marsh, J.M.; Whitaker, S.; Felts, T.; Shearouse, W.; Vatter, M.; Määttä, A.; Thompsonm, M.; Hawkins, T.J. Role of Internal Lipids in Hair Health. *J. Cosmet. Sci.* **2018**, *69*, 347–356.
4. Förster, T.; Issberner, U.; Hensen, H. Lipid/surfactant compounds as a new tool to optimize skin-care properties of personal-cleansing products. *J. Surfactants Deterg.* **2000**, *3*, 345–352. [CrossRef]
5. Song, S.; Lim, J.Y.; Son, S.K.; Choi, J.; Kang, N.; Lee, S. Prevention of lipid loss from hair surface and internal modification. *Sci. Rep.* **2019**, *9*, 9834.
6. Joo, K.-M.; Kim, A.-R.; Kim, S.-N.; Kim, B.-M.; Lee, H.K.; Bae, S.; Lee, J.-H.; Lim, K.-M. Metabolomic analysis of amino acids and lipids in human hair altered by dyeing, perming and bleaching. *Exp. Dermatol.* **2016**, *25*, 729–731. [CrossRef] [PubMed]
7. Bantignies, J.L.; Fuchs, G.; Carr, G.L.; Williams, G.P.; Lutz, D.; Marull, S. Organic reagent interaction with hair spatially characterized by infrared microspectroscopy using synchrotron radiation. *Int. J. Cosmet. Sci.* **1998**, *20*, 381–394. [CrossRef]
8. Breakspear, S.; Smith, J.R.; Luengo, G. Effect of the covalently linked fatty acid 18-MEA on the nanotribology of hair's outermost surface. *J. Struct. Biol.* **2005**, *149*, 235–242. [CrossRef]
9. Hilterhaus-Bong, S.; Zahn, H. Contributions to the chemistry of human hair: II. Lipid chemical aspects of permanently waved hair. *Int. J. Cosmet. Sci.* **1989**, *11*, 167–174. [CrossRef]
10. Csuka, D.A.; Csuka, E.A.; Juhász, M.L.; Sharma, A.N.; Mesinkovska, N.A. A systematic review on the lipid composition of human hair. *Int. J. Dermatol.* **2023**, *62*, 404–415. [CrossRef]
11. Clay, C.; Cook, K.; Rough, J.I. Studies in the composition of human hair. *J. Am. Chem. Soc.* **1940**, *62*, 2709–2710. [CrossRef]
12. Simmonds, D.H. The amino acid composition of keratins. *Text. Res. J.* **1958**, *28*, 314–317. [CrossRef]
13. Robbins, C.R.; Kelly, C.H. Amino acid composition of human hair. *Text. Res. J.* **1970**, *40*, 891–896. [CrossRef]
14. Robbins, C.R. Chemical aspects of bleaching human hair. *J. Soc. Cosmet. Chem.* **1971**, *22*, 339–348.
15. Tanaka, S.; Imura, H.; Sugiyama, T. Study of the test method of reduction and recovery of disulfide bond in human hair. *J. Soc. Cosmet. Chem. Jpn.* **1992**, *25*, 232–239. [CrossRef]
16. Lee, W.S.; Oh, T.H.; Chun, S.H. Integral lipid in human hair follicle. *J. Investig. Dermatol. Symp. Proc.* **2005**, *10*, 234–237. [CrossRef]
17. Coderch, L.; Oliver, M.A.; Martínez, V.; Manich, A.M.; Rubio, L.; Martí, M. Exogenous and endogenous lipids of human hair. *Skin. Res. Technol.* **2017**, *23*, 479–485. [CrossRef]
18. Naito, S.; Ooshika, M.; Yorinoto, N.; Kuroda, Y. The structure of bound lipids of human hair fibers and its physical properties. *Proc. 9th Int. Wool Text. Res. Conf. Biella, Italy* **1995**, *2*, 367–374.
19. Marcott, C.; Lo, M.; Kjoller, K.; Fiat, F.; Baghdadli, N.; Balooch, G.; Luengo, G. Localization of human hair structural lipids using nanoscale infrared spectroscopy and imaging. *Appl. Spectrosc.* **2014**, *68*, 564–569. [CrossRef]
20. Zhang, G.; Senak, L.; Moore, D.J. Measuring changes in chemistry, composition, and molecular structure within hair fibers by infrared and Raman spectroscopic imaging. *J. Biomed. Opt.* **2011**, *16*, 056009. [CrossRef]
21. Kreplak, L.; Briki, F.; Duvault, Y.; Doucet, J.; Merigoux, C.; Leroy, F.; Lévêque, J.L.; Miller, L.; Carr, G.L.; Williams, G.P.; et al. Profiling lipids across Caucasian and Afro-American hair transverse cuts, using synchrotron infrared microspectrometry. *Int. J. Cosmet. Sci.* **2001**, *23*, 369–374. [CrossRef]
22. Wertz, P.W.; Downing, D.T. Integral lipids of human hair. *Lipids* **1988**, *23*, 878–881. [CrossRef]
23. Ryu, H.K.; Jung, B.H.; Kim, K.M.; Yoo, E.A.; Woo, J.-T.; Chung, B.C. Determination of cholesterol in human hair using gas chromatography-mass spectrometry. *Biomed. Chromatogr.* **2006**, *20*, 999–1003. [CrossRef]
24. Robbins, C.R. *Chemical and Physical Behavior of Human Hair*; Springer: Berlin/Heidelberg, Germany, 2012. [CrossRef]
25. Okamoto, M.; Ishikawa, K.; Tanji, N.; Aoyagi, S.; Kita, I.; Migita, C.T. Structural analysis of the outermost hair surface using TOF-SIMS with C60 depth profiling technique. *E-J. Surf. Sci. Nanotechnol.* **2012**, *10*, 234–238. [CrossRef]

26. Lshikawa, K.; Okamotoy, M.; Aoyag, S. Structural analysis of the outermost hair surface using TOF-SIMS with gas cluster ion beam sputtering. *Biointerphases* **2016**, *11*, 02A315. [CrossRef]
27. Rogers, G.E. Known and unknown features of hair cuticle structure: A brief review. *Cosmetics* **2019**, *6*, 32. [CrossRef]
28. Fellows, A.P.; Casford, M.T.L.; Davies, P.B. Nanoscale molecular characterization of hair cuticle cells using integrated atomic force microscopy-infrared laser spectroscopy. *Appl. Spectrosc.* **2020**, *74*, 1540–1550. [CrossRef] [PubMed]
29. Destaillats, F.; Guitard, M.; Cruz-Hernandez, C. Identification of D6-monounsaturated fatty acids in human hair and nail samples by gas-chromatography-mass-spectrometry using ionic-liquid coated capillary column. *J. Chromatogr. A* **2011**, *1218*, 9384–9389. [CrossRef]
30. Takahashi, T.; Yoshida, S. A highly resistant structure between cuticle and cortex of human hair. *Int. J. Cosmet. Sci.* **2017**, *39*, 327–336. [CrossRef]
31. Takahashi, T.; Yoshida, S. Distribution of glycolipid and unsaturated fatty acids in human hair. *Lipids* **2014**, *49*, 905–917. [CrossRef]
32. Dawber, R. Hair: Its structure and response to cosmetic preparations. *Clin. Dermatol.* **1996**, *14*, 105–112. [CrossRef]
33. Fellows, A.P.; Casford, M.T.; Davies, P.B. Using hybrid atomic force microscopy and infrared spectroscopy (AFM-IR) to identify chemical components of the hair medulla on the nanoscale. *J. Microsc.* **2021**, *284*, 189–202. [CrossRef] [PubMed]
34. Barba, C.; Oliver, M.A.; Martí, M.; Kreuzer, M.; Coderch, L. Lipid distribution on ethnic hairs by Fourier transform infrared synchrotron spectroscopy. *Skin. Res. Technol.* **2022**, *28*, 75–83. [CrossRef] [PubMed]
35. Ymazaki, J.; Maeda, K. Analysis of lipids in the medulla of Japanese hair and their function. *Cosmetics* **2018**, *5*, 27. [CrossRef]
36. Kaneta, D.; Goto, M.; Hagihara, M.; Leproux, P.; Couderc, V.; Egawa, M.; Kano, H. Visualizing intra-medulla lipids in human hair using ultra-multiplex CARS, SHG, and THG microscopy. *Analyst* **2021**, *146*, 1163–1168. [CrossRef]
37. Sandt, C.; Borondics, F. A new typology of human hair medullas based on lipid composition analysis by synchrotron FTIR microspectroscopy. *Analyst* **2021**, *146*, 3942–3954. [CrossRef]
38. Negri, A.P.; Cornell, H.J.; Rivett, D.E. A model for the surface of keratin fibers. *Text Res. J.* **1993**, *63*, 109–115.
39. Swift, J.A. Human hair cuticle: Biologically conspired to the owner's advantage. *J. Cosmet. Sci.* **1999**, *50*, 23–47.
40. Luengo, G.; Schmitt, F.J.; Hill, R.; Israelachvili, J. Thin film rheology and tribology of confined polymer melts: Contrast with bulk properties. *Macromolecules* **1997**, *30*, 2482–2494. [CrossRef]
41. Zahn, H.; Messenger, H.; Hocker, H. Covalently linked fatty acids at the surface of wool: Part of the cuticle cell envelope. *Text. Res. J.* **1994**, *64*, 554–555. [CrossRef]
42. Robbins, C.R. The cell membrane complex: Three related but different cellular cohesion components of mammalian hair fibers. *J. Cosmet. Sci.* **2009**, *60*, 437–465. [CrossRef]
43. Naito, S.; Takahashi, T.; Hattori, M.; Arai, K. Histochemical observation of the cell membrane complex of hair. *Sen-I Gakkaishi* **1992**, *48*, 420–426. [CrossRef] [PubMed]
44. Sideris, V.; Holt, L.A.; Leaver, I.H. A microscopical study of the pathway for diffusion of rhodamine B and octadecylrhodamine B into wool fibers. *J. Soc. Dyers Color.* **1990**, *106*, 131–135. [CrossRef]
45. Nishimura, K.; Nishino, M.; Inaoka, Y.; Kitada, Y.; Fukushima, M. Interrelationship between the hair lipids and the hair moisture. *Nippon. Koshohin Kagakkaishi* **1989**, *13*, 134–139.
46. Philippe, M.; Garson, J.C.; Gilard, P.; Hocquaux, M.; Hussler, G.; Leroy, F.; Mahieu, C.; Semeria, D.; Vanlerberghe, G. Synthesis of 2-N-oleoylamino-octadecane-1,3-diol: A new ceramide highly effective for the treatment of skin and hair. *Int. J. Cosmet. Sci.* **1995**, *17*, 133–146. [CrossRef] [PubMed]
47. Jones, L.N.; Rivett, D.E. 18-Methyleicosanoic acid in the structure and formation of mammalian hair fibres. *Micron* **1997**, *28*, 469–485. [CrossRef] [PubMed]
48. Coderch, L.; Méndez, S.; Barba, C.; Pons, R.; Martí, M.; Parra, J.L. Lamellar rearrangement of internal lipids from human hair. *Chem. Phys. Lipids* **2008**, *155*, 1–6. [CrossRef]
49. Smith, J.; Swift, J. Maple syrup urine disease hair reveals the importance of 18-methyleicosanoic acid in cuticular delamination. *Micron* **2005**, *36*, 261–266. [CrossRef]
50. Ishihara, A.; Tsukamoto, Y.; Inoue, H.; Noda, Y.; Koizumi, S.; Joko, K. Analysis of water distribution in delipidated human hair by small-angle neutron scattering (SANS). *Int. J. Cosmet. Sci.* **2021**, *43*, 653–661. [CrossRef]
51. Evans, T. Measuring the water content of hair. *Cosmet. Toil* **2014**, *129*, 1–5.
52. Duvel, L.; Chun, H.; Deppa, D.; Wertz, P.W. Analysis of hair lipids and tensile properties as a function of distance from scalp. *Int. J. Cosmet. Sci.* **2005**, *27*, 193–197. [CrossRef]
53. Coderch, L.; Oliver, M.A.; Carrer, V.; Manich, A.M.; Martí, M. External lipid function in ethnic hairs. *J. Cosmet. Dermatol.* **2019**, *18*, 1912–1920. [CrossRef] [PubMed]
54. Tanamachi, H.; Tokunaga, S.; Tanji, N.; Oguri, M.; Inoue, S. 18-MEA and hair appearance. *J. Cosmet. Sci.* **2010**, *61*, 147–160.
55. Daniels, G.; Fraser, A.; Westgate, G.E. How different is human hair? A critical appraisal of the reported differences in global hair fibre characteristics and properties towards defining a more relevant framework for hair type classification. *Int. J. Cosmet. Sci.* **2023**, *45*, 50–61. [CrossRef]
56. Martí, M.; Barba, C.; Manich, A.M.; Rubio, L.; Alonso, C.; Coderch, L. The influence of hair lipids in ethnic hair properties. *Int. J. Cosmet. Sci.* **2016**, *38*, 77–84. [CrossRef] [PubMed]
57. Oliver, M.A.; Coderch, L.; Carrer, V.; Barba, C.; Martí, M. Ethnic hair: Thermoanalytical and spectroscopic differences. *Skin. Res. Technol.* **2020**, *26*, 617–626. [CrossRef]

58. Bildstein, L.; Deniset-Besseau, A.; Pasini, I.; Mazilier, C.; Keuong, Y.W.; Dazzi, A.; Baghdadli, N. Discrete nanoscale distribution of hair lipids fails to provide humidity resistance. *Anal. Chem.* **2020**, *92*, 11498–11504. [CrossRef]
59. Cruz, C.F.; Fernandes, M.M.; Gomes, A.C.; Coderch, L.; Martí, M.; Méndez, S.; Gales, L.; Azoia, G.G.; Shimanovich, U.; Cavaco-Paulo, A. Keratins and lipids in ethnic hair. *Int. J. Cosmet. Sci.* **2013**, *35*, 244–249. [CrossRef]
60. Maymone, M.B.; Laughter, M.; Pollock, S.; Khan, I.; Marques, T.; Abdat, R.; Vashi, N.A. Hair aging in different races and ethnicities. *J. Clin. Aesthetic Dermatol.* **2021**, *14*, 38.
61. Van Wicklin, S.A. Hair Aging in Different Races and Ethnicities. *Plast. Aesthetic Nurs.* **2023**, *43*, 56–60. [CrossRef] [PubMed]
62. Oliver, M.A.; Martí, M.; Coderch, L.; Carrer, V.; Kreuzer, M.; Barba, C. Lipid loses and barrier function modifications of the brown-to-white hair transition. *Skin. Res. Technol.* **2019**, *25*, 517–525. [CrossRef]
63. Lee, Y.; Kim, Y.D.; Pi, L.-Q.; Lee, S.Y.; Hong, H.; Lee, W.-S. Comparison of hair shaft damage after chemical treatment in Asian, White European, and African hair. *Int. J. Dermatol.* **2014**, *53*, 1103–1110. [CrossRef] [PubMed]
64. Masukawa, Y.; Tsujimura, H.; Narita, H. Liquid chromatographymass spectrometry for comprehensive profiling of ceramide molecules in human hair. *J. Lipid Res.* **2006**, *47*, 1559–1571. [CrossRef] [PubMed]
65. Coderch, L.; Lorenzo, R.D.; Mussone, M.; Alonso, C.; Martí, M. The Role of Lipids in the Process of Hair Ageing. *Cosmetics* **2022**, *9*, 124. [CrossRef]
66. Takahashi, T.; Mamada, A.; Breakspear, S.; Itou, T.; Tanji, N. Age-dependent changes in damage processes of hair cuticle. *J. Cosmet. Dermatol.* **2015**, *14*, 2–8. [CrossRef]
67. Vyumvuhore, R.; Verzeaux, L.; Gilardeau, S.; Bordes, S.; Aymard, E.; Manfait, M.; Closs, B. Investigation of the molecular signature of greying hair shafts. *Int. J. Cosmet. Sci.* **2021**, *14*, 2–8. [CrossRef]
68. Ma, Y.; He, C. Exploration of potential lipid biomarkers for age-induced hair graying by lipidomic analyses of hair shaft roots with follicular tissue attached. *J. Cosmet. Dermatol.* **2022**, *21*, 6118–6123. [CrossRef] [PubMed]
69. Habe, T.; Tanji, N.; Inoue, S.; Okamoto, M.; Tokunaga, S.; Tanamachi, H. ToF-SIMS characterization of the lipid layer on the hair surface. I: The damage caused by chemical treatments and UV radiation. *Surf. Interface Anal.* **2011**, *43*, 410–412. [CrossRef]
70. Ji, J.H.; Park, T.S.; Lee, H.-J.; Kim, Y.-D.; Pi, L.-Q.; Jin, X.-H.; Lee, W.-S. The ethnic differences of the damage of hair and integral hair lipid after ultra violet radiation. *Ann. Dermatol.* **2013**, *25*, 54–60. [CrossRef]
71. Richena, M.; Rezende, C.A. Structure of photo-damaged white and naturally pigmented human hair. *J. Photochem. Photobiol. B Biol.* **2020**, *202*, 111673. [CrossRef]
72. Ross, A.B.; Maes, E.; Lee, E.J.; Homewood, I.; Marsh, J.M.; Davis, S.L.; Willicut, R.J. UV and visible light exposure to hair leads to widespread changes in the hair lipidome. *Int. J. Cosmet. Sci.* **2022**, *44*, 672–684. [CrossRef]
73. Sandt, C.; Borondics, F. Super-resolution infrared microspectroscopy reveals heterogeneous distribution of photosensitive lipids in human hair medulla. *Talanta* **2023**, *254*, 124152. [CrossRef]
74. Tokunaga, S.; Tanamachi, H.; Ishikawa, K. Degradation of hair surface: Importance of 18-MEA and epicuticle. *Cosmetics* **2019**, *6*, 31. [CrossRef]
75. Reis, M.F.; Dias, G. Hair Cosmetics: An Overview. *Int. J. Trichology* **2015**, *7*, 2–15.
76. Deeksha; Malviya, R.; Sharma, P.K. Advancement in shampoo (a dermal care product): Preparation methods, patents and commercial utility. *Recent. Pat. Inflamm. Allergy Drug Discov.* **2014**, *8*, 48–58. [CrossRef]
77. Draelos, Z.D. Essentials of Hair Care often Neglected: Hair Cleansing. *Int. J. Trichology* **2010**, *2*, 24–29. [CrossRef]
78. Robbins, C.R. Chapter 6. Interactions of Shampoo and Conditioner Ingredients with Hair. In *Chemical and Physical Behavior of Human Hair*, 5th ed.; Springer: Berlin/Heidelberg, Germany, 2012; pp. 329–436.
79. Ajayi, O.; Davies, A.; Amin, S. Impact of Processing Conditions on Rheology, Tribology and Wet Lubrication Performance of a Novel Amino Lipid Hair Conditioner. *Cosmetics* **2021**, *8*, 77. [CrossRef]
80. Luengo, G.S.; Fameau, A.L.; Leonforte, F.; Greaves, A.J. Surface science of cosmetic substrates, cleansing actives and formulations. *Adv. Colloid Interface Sci.* **2021**, *290*, 102383. [CrossRef]
81. Fernandes, C.; Medronho, B.; Alves, L.; Rasteiro, M.G. On Hair Care Physicochemistry: From Structure and Degradation to Novel Biobased Conditioning Agents. *Polymers* **2023**, *15*, 608. [CrossRef]
82. La Torre, C.; Bhushan, B. Nanotribological effects of silicone type, silicone deposition level, and surfactant type on human hair using atomic force microscopy. *J. Cosmet. Sci.* **2006**, *57*, 37–56.
83. Nazir, H.; Lv, P.; Wang, L.; Lian, G.; Zhu, S.; Ma, G. Uniform-sized silicone oil microemulsions: Preparation, investigation of stability and deposition on hair surface. *J. Colloid. Interface Sci.* **2011**, *364*, 56–64. [CrossRef]
84. Nazir, H.; Wang, L.; Lian, G.; Zhu, S.; Zhang, Y.; Liu, Y.; Ma, G. Multilayered silicone oil droplets of narrow size distribution: Preparation and improved deposition on hair. *Colloids Surf. B Biointerfaces* **2012**, *10*, 42–49. [CrossRef] [PubMed]
85. O'Lenick, T. Anionic/cationic complexes in hair care. *J. Cosmet. Sci.* **2011**, *62*, 209–228. [PubMed]
86. Kourbaj, G.; Bielfeldt, S.; Kruse, I.; Wilhelm, K.P. Confocal Raman spectroscopy is suitable to assess hair cleansing-derived skin dryness on human scalp. *Ski. Res. Technol.* **2022**, *28*, 577–581. [CrossRef] [PubMed]
87. Shaw, D.A. Hair lipid and surfactants. Extraction of lipid by surfactants and lack of effect of shampooing on rate of re-fatting of hair. *Int. J. Cosmet. Sci.* **1979**, *1*, 317–328. [CrossRef]
88. Koch, J.; Aitzetmuller, K.; Bittorf, G.; Waibel, J. Hair lipids and their contribution to the perception of hair oiliness. Part I: Surface and internal lipids in hair. *J. Soc. Cosmet. Chem.* **1982**, *33*, 317–326.
89. Capablanca, J.S.; Watt, I. Factors affecting the zeta potential at wool fiber surfaces. *Text. Res. J.* **1986**, *56*, 49–55. [CrossRef]

90. Zhang, Y.; Alsop, R.J.; Soomro, A.; Yang, F.C.; Rheinstädter, M.C. Effect of shampoo, conditioner and permanent waving on the molecular structure of human hair. *PeerJ* **2015**, *3*, e1296. [CrossRef]
91. Masukawa, Y.; Tsujimura, H. Highly sensitive determination of diverse ceramides in human hair using reversed-phase high performance liquid chromatography-electrospray ionization mass spectrometry. *Lipids* **2007**, *42*, 275–290. [CrossRef]
92. Masukawa, Y.; Tsujimura, H.; Tanamachi, H.; Narita, H.; Imokawa, G. Damage to human hair caused by repeated bleaching combined with daily weathering during daily life activities. *Exog. Dermatol.* **2004**, *3*, 273–281. [CrossRef]
93. Song, S.-H.; Son, S.K.; Kang, N.-G. Archives of clinical and medical case reports 573 case report dual case reports for lipid loss from human hair. *Arch. Clin. Med. Case Rep.* **2019**, *53*, 1103–1110.
94. Marsh, J.M.; Brown, M.A.; Felts, T.J.; Hutton, H.D.; Vatter, M.L.; Whitaker, S.; Wireko, F.C.; Styczynski, P.B.; Henry, I.D. Gel network shampoo formulation and hair health benefits. *Int. J. Cosmet. Sci.* **2017**, *39*, 543–549. [CrossRef] [PubMed]
95. Šindelka, K.; Kowalski, A.; Cooke, M.; Mendoza, C.; Lísal, M. Interactions of cationic surfactant-fatty alcohol monolayers with natural human hair surface: Insights from dissipative particle dynamics. *J. Mol. Liq.* **2023**, *375*, 121385. [CrossRef]
96. Ahmad, A.; Ahsan, H. Lipid-based formulations in cosmeceuticals and biopharmaceuticals. *Biomed. Dermatol.* **2020**, *4*, 12. [CrossRef]