Chapter 7

Latent fingermark aging: chemical degradation over time

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Abstract

This chapter aims at presenting an overview of the current knowledge regarding the chemical composition of fingermarks and its modification as a function of time, focusing primarily on the compounds targeted in fingermark detection and/or age estimation purposes. As numerous studies have been published regarding these constituents in various contexts, this discussion will pertain mainly to fingermarks and human skin secretions, with some *in vitro* experiments where relevant additional information is provided.

Thus, chemical degradation of the main eccrine (e.g. water, amino acids, proteins, lactic acid) and sebaceous (e.g. fatty acids, triglycerides, wax esters) components will be detailed, including illustrations of molecular structures, degradation mechanisms and products. Four main factors affecting the chemical degradation of fingermark components will also be described, namely the initial chemical composition (i.e. variations due to interactions between fingermark components, donors' characteristics and transfer conditions), the nature of the substrate, the environment (i.e. variations due to light, air flow, water and ambient humidity, temperature and microbial activity) and time. Finally, key elements to be considered when conducting fingermark aging studies will be discussed.

Keywords

Eccrine, sebaceous, amino acids, lipids, fatty acids, squalene, oxidation, ozonolysis, donor variation, deposition, environment, fingerprints

Acronym list

ChOOH:	Hydroperoxycholesterol
FA:	Fatty Acid
FTIR:	Fourier Transform Infrared
GC-MS:	Gas Chromatography-Mass Spectrometry
LC-MS:	Liquid Chromatography-Mass Spectrometry
MALDI-MS:	Matrix-Assisted Laser Desorption/Ionisation-Mass Spectrometry
ORO:	Oil Red O
SQ:	Squalene
TG:	Triglyceride
TOP:	4,8,13,17,21-Tetra-methyl-Octadeca-4,8,12,16,20-Pentaene-al
TOT:	4,9,13,17-Tetramethyl-Octadeca-4,8,12,16-Tetraeneal
TTT:	5,9,13-Trimethyl-Tetradeca-4,8,12-Triene-al
UHPLC-HRAM Orbitrap™ MS:	UltraHigh-Performance Liquid Chromatography-High Resolution Accurate Mass Orbitrap™ Mass Spectrometry
UPLC-IMS-QToF-MS^E:	Ultra-Performance Liquid Chromatography-Ion Mobility Spectroscopy-Quadrupole Time-Of-Flight Mass Spectrometry

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7.1 Introduction

After deposition on a surface, the residue that constitutes a latent fingermark is susceptible to a number of chemical (as well as physical) modifications. The nature and rates of these processes can have a significant impact on the persistence of target compounds, and hence detectability, but may also provide a basis for estimating the age of a latent fingermark. The idea of estimating fingermark age dates back at least to the early 20th century [1], with the first reported fingermark dating approaches published in the 1960s (to the best of the authors' knowledge) [2, 3]. However, early propositions based on the study of chemical modifications did not show reproducible results [3-8] or were often based on facile observations such as the appearance of a fingermark after powdering [9-11]. In addition to being unreliable, methods based on such physical modifications of fingermarks have little to no basis in any understanding of the relevant aging processes involved, and the fact that excellent ridge quality was often observed from old fingermarks can be difficult to explain in an informed manner [12, 13]. With continuing advances in analytical technology, several investigations into the chemical changes in latent fingermark composition over time have been reported in recent decades, with a focus on several broad goals:

1) Understanding how aging and environmental factors impact the detection of latent fingermarks [14-17]
2) Identification of stable products as potential targets for fingermark detection [14, 16, 18]
3) Modelling of target compound aging, towards the development of a reliable method for latent fingermark age estimation [19-26]

This chapter provides an overview of the current state of the literature regarding chemical modifications undergone by latent fingermark constituents as a function of time, with a primary focus on compounds of particular relevance to fingermark detection and/or studies into the development of methods for age estimation. This is followed by a discussion of the factors that can influence fingermark residue degradation, and so must be taken into account in any attempt to estimate fingermark age. Owing to the substantial number of compounds present in latent fingermarks and the large volume of information regarding their reactivity in various matrices, this overview will focus on studies pertaining to latent fingermarks and human skin secretions, although discussion of *in vitro* experiments is included where appropriate.

7.2 Chemical degradation of eccrine components

The earliest reported works into the effects of aging on fingermark composition focused on the eccrine components targeted by detection methods, i.e. chloride [3], as well as amino acids and other nitrogenous components such as urea [27]. The key aim of Cuthbertson and Morris's investigations were to investigate the effects of compositional variation on fingermark detection, but the possibility of estimating the age was also highlighted, based on changes seen detected in the concentrations of these compounds as a function of time following deposition.

The aging of eccrine components is of particular relevance due to the fact that eccrine glands are present along the ridges of the fingertips, and so their secretions are the most likely to be present in latent fingermarks. Besides water, salts and small organic compounds, eccrine glands secrete several large organic molecules (e.g. peptides and proteins), the behaviour of which over time may provide interesting results for the development of fingermark dating methodologies, particularly over longer time periods (e.g. up to several months or even years). The following sections describe several of the main eccrine compounds found in fingermark residue and their degradation processes (where known).

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7.2.1 Water

While not strictly a chemical process, the evaporation of water is one of the first processes that occurs after fingermark deposition, and its loss thereby alters the initial chemical composition of the latent residue, as well as its physical properties. Water comprises approximately 99 % of eccrine sweat, but the actual water content of latent fingermarks can vary considerably (20 – 70 %), depending on factors such as the amount of eccrine secretions present on the ridge skin at the time of deposition, and the presence of other constituents such as sebaceous lipids or exogenous substances such as food [28, 29].

A rapid decrease in mass that occurs soon after deposition has been observed in several investigations into fingermark composition and aging, and has often been attributed primarily to the volatilisation of water, as well as low molecular weight organic constituents [16, 30, 31]. Recently, Keisar *et al*. utilised temperature-programmed desorption-mass spectrometry in combination with mass measurements using a quartz crystal microbalance to confirm whether this short-term mass loss was due solely to water evaporation [29]. When fingermarks were kept at 37 °C, water evaporation occurred within minutes following deposition, with samples from unwashed hands (containing some lipid material) exhibiting a slower mass loss rate.

7.2.2 Amino acids and proteins

Free amino acids, which are the targets of several fingermark detection methods such as ninhydrin and 1,2-indanedione, are often considered to be relatively stable fingermark components. Fingermark detection with amino acid-sensitive reagents has been successfully carried out on porous substrates known to be several decades to over a century old [9, 32]. It is therefore widely assumed that as long as paper substrates are not exposed to elevated humidity or immersion in water, thereby dissolving the amino acids from the latent residue, the amino acids remain stably bonded to the cellulose fibres [32]. However, work by Cuthbertson and Morris indicates that (at least some) amino acids do undergo some kind of degradation process over time, as the total mass of amino acids decreased significantly over 236 days after deposition on aluminium [27]. The reaction pathway(s) involved in this process have not yet been identified. This degradation process is considered a slow one, as the effectiveness of amino acid-sensitive reagents on older specimens has been proven several times [33].

Other studies into amino acid degradation in latent fingermarks have focused on the effects of temperature, in order to simulate the effects of extreme temperatures (400 – 500 °C) that would be produced during combustion, e.g. in cases of arson or explosions [18]. Under these conditions, alanine was observed to undergo condensation to produce dimethylpiperazine-2,5-dione, while aspartic acid decomposed to form maleimide and 2,5-furandione. Pyrolysis products of other abundant eccrine amino acids, such as serine, glycine, and lysine, were not observed. De Paoli *et al*. similarly observed that amino acids (aspartic acid, glutamic acid, glycine, histidine, ornithine, serine and threonine) in solution underwent thermal degradation at 100 – 150 °C, but were unable to detect any degradation products using liquid chromatography-mass spectrometry (LC-MS) [34].

Van Dam *et al*. proposed a method of age estimation based on the autofluorescence of aged fingermarks, which was attributed to an unspecified complex formed between tryptophan-containing proteins and oxidised lipid material [35]. Later investigations utilising thin layer chromatography indicated that protein-bound tryptophan in fact degrades to produce a number of fluorescent

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derivatives, including indoleacetic acid, β-carbolines and xanthurenic acid (Figure 1), possibly as a result of bacterial activity [36].

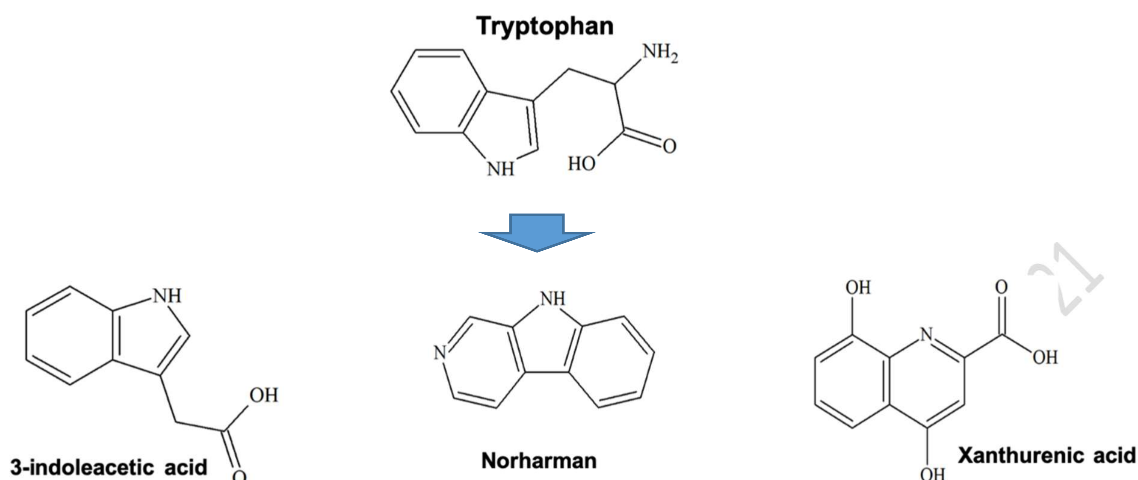

Figure 1: Molecular structures of tryptophan and its fluorescent degradation products

In an investigation into compositional variation, van Helmond *et al.* tentatively identified a series of endogenous amino acid degradation products in fingermarks, including urocanic acid, pyroglutamic acid and 4-methylene-l-glutamine, based on accurate mass measurements [37]. Urocanic acid is produced by the deamination of histidine, while the other two are derived from glutamine. It was observed that the relative quantities of these compounds were greater in natural fingermarks (sample collected without prior preparation of the fingertip skin by cleaning and can include substances from incidental touching of body parts, objects and other chemical/biological products) than eccrine samples. This may be indicative of the longer time the precursor amino acids had been present on the fingertips, compared to the eccrine samples, indicating that these possible degradation processes take place on the skin surface [37].

Until recently, fingermark proteins remained overlooked in comparison to free amino acids. Oonk *et al*. studied the aging of target proteins utilising a proteomics-based approach [21]. From a pool of identified proteins, five, including several keratins and dermcidin, were selected as potential markers for fingermark age determination. Dermcidin was found to decrease in signal over 16 days at ambient temperature (20 °C). Conversely, the keratins showed a relative increase, which was attributed to the degradation of less stable protein constituents. It should be noted that the investigation of degradation pathways was beyond the scope of this study, and so no degradation products have yet been identified.

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7.2.3 Other eccrine components

There are a number of other eccrine constituents that undergo degradation, though many of these are less relevant to fingermark detection than those described above. One exception is lactic acid, which is a target of cyanoacrylate fuming. De Paoli *et al*. reported that lactic acid photooxidises to pyruvate at 50 °C with simulated sunlight exposure (Figure 2) [34]. Both lactic acid and pyruvate were shown to decompose at 50 °C. Wargacki *et al*. inferred that this process is responsible for the poor performance of cyanoacrylate fuming on fingermarks that have been exposed to light and air for one day following deposition [38]. However, further studies on the degradation of lactic acid in fingermark

residue and its effect on detection techniques have not been reported, and so this hypothesis is not yet confirmed.

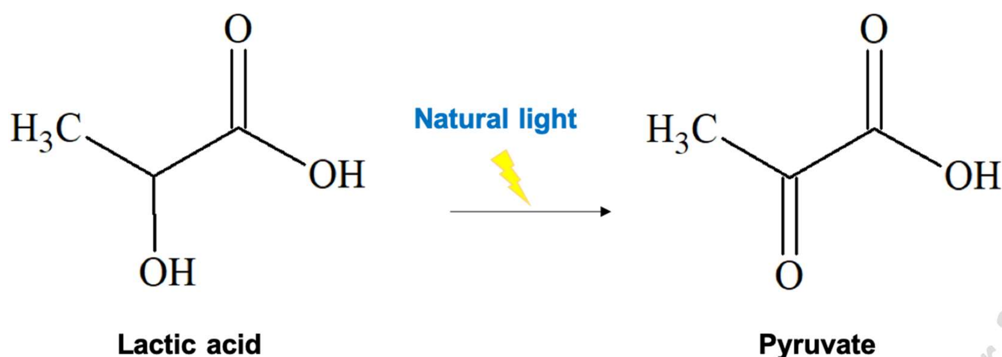

Figure 2: Molecular structures of lactic acid and pyruvate

Ammonia and urea were part of an investigation into fingermark composition and degradation in the 1970s, as it was thought that nitrogen-containing components might be chemically altered by bacteria, and hence provide a means to estimate fingermark age [2]. Cuthbertson and Morris observed that both compounds underwent a quantitative decrease over 236 days [27]. However, this degradation did not appear to be reproducible, due to sample variation and donor-dependent degradation rates. More recently, De Paoli *et al*. reported that urea standards were thermally degraded at 150 °C, but appeared unaffected by photodegradation [34].

Generally, studies on the degradation processes of the eccrine components, even of key target compounds, for the development of detection or age estimation methods, are rather limited. Latent fingermarks contain a number of other eccrine constituents in addition to those discussed above, such as B-complex vitamins [6], phenol [39], uric acid and creatinine [40]. Thus, further research focusing on these components may be of interest in regard to their degradation and potential markers for age estimations.

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7.3 Chemical degradation of sebaceous components

The aging processes of the water-insoluble fraction of latent fingermarks, of which lipids are a subgroup, are relevant to a variety of fingermark detection techniques. This is particularly true in instances where substrates have been wetted, and eccrine constituents may have been removed [41, 42]. Sebum is a major source of fingermark lipids and contains a number of unsaturated compounds that are susceptible to chemical modifications soon after deposition, making them attractive as potential targets for age estimation. Many studies into fingermark aging have focused on specific sebaceous lipids or lipid classes, such as squalene, fatty acids and glycerides [15, 23, 24, 43, 44]. However, it must be noted that the sebaceous lipids in fingermark residue originate from transfer through physical contact of the fingertips with body parts such as the face or hair, thus the amount present can vary to a greater extent than eccrine compounds. This may explain some of the (quantitative) variability observed among fresh fingermark residue from the same person (intra-individual variation) and is an important issue to overcome for age estimation purposes.

Concerning the general behaviour over time of lipids found in fingermark residue, Mong *et al*. observed that older fingermark residue appears to solidify, and therefore become less receptive to staining by histological dyes [45]. These changes are consistent with the increase in viscosity that

occurs with the progressive oxidation of various unsaturated sebaceous lipids, including squalene and glycerides, as well as the evaporation of volatile organic compounds produced by these processes.

Outside of the forensic literature, indications as to the degradation processes undergone in latent fingermark residue may be found in fields such as dermatology and air quality research. Oxidation of skin surface lipids, including squalene, cholesterol and unsaturated fatty acids, has been observed to take place *in situ* [46-50], and provides a complement to the more preliminary information gained so far based on fingermark samples. The following sections provide an overview of the current state of knowledge regarding the degradation of the sebaceous lipids present in fingermark residue.

7.3.1 Free fatty acids (FAs) and triglycerides (TGs)

A study by Archer *et al*. reported that most free fatty acids in latent fingermarks appeared to undergo an initial increase in concentration, followed by a subsequent decrease over 33 days following sample collection [15, 51]. They hypothesised that there might be competing mechanisms of fatty acid generation and degradation, such as the hydrolysis of triglycerides; however, neither glycerides nor proposed degradation products could be identified using gas chromatography-mass spectrometry (GC-MS). Other researchers have reported the degradation of unsaturated free fatty acids with increasing fingermark age over comparable aging times [16, 23]; however, the observation described by Archer *et al*. has not been replicated. It should be noted that this trend was not significant in a majority of the samples [15]. Weyermann *et al*. found high variability in free fatty acid concentrations over 1 month and thus, no significant trends could be determined [44], while other investigations have described that unsaturated fatty acids appear to be significantly affected by aging processes [16, 52].

Mong *et al*. proposed that 'air oxidation' of unsaturated fatty acids involved cleavage at the double bond [16] after observing that aged fingermarks contained several short chain fatty acids as well as dicarboxylic acids. As an example, they suggested nonanoic acid and nonanedioic acid as oxidation products of oleic acid (FA 18:1Δ9). Work by Pleik *et al*. identified similar degradation products derived from FA 16:1 and FA 18:1 over 14 days of aging using GC-MS, but pointed out that cleavage at the double bond yielded different degradation products in fingermark samples compared to the Δ9 unsaturated fatty acid standards [23]. These results enabled them to definitively conclude that the fatty acids in latent fingermarks were sapienic acid (FA 16:1Δ6) and FA 18:1Δ8. Ozonolysis of these fatty acids results in the formation of decanal, and oxohexanoic acid and oxooctanoic acid (from FA 16:1Δ6 and FA 18:1Δ8, respectively). These can be oxidised further to form decanoic acid, as well as dicarboxylic acids (i.e. hexanedioic acid and octanedioic acid) [23]. Figure 3 provides a summary of this process. Similar products will be formed from other unsaturated free fatty acids, depending on total chain length and double bond position.

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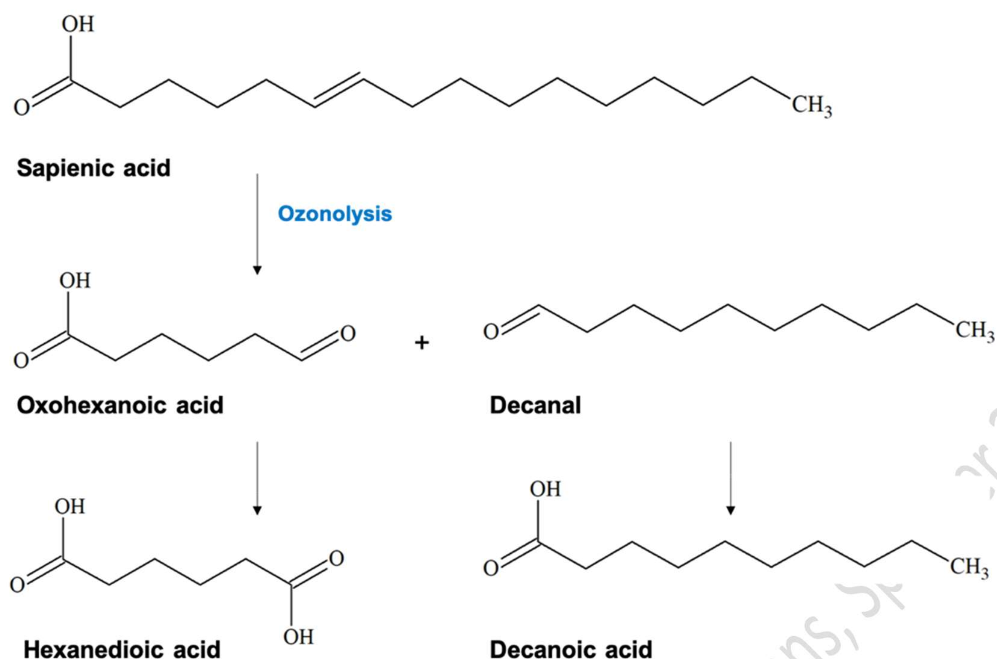

Figure 3: Degradation of sapienic acid (FA 16:1Δ6)

It has been proposed that the oxidation of fingermark glycerides occurs via similar processes to drying oils such as linseed oil, which undergoes autoxidation to form hydroperoxides, as well as polymerisation [16]; though these processes have never been directly observed in fingermark residue. Johnston and Rogers inferred, based on Fourier transform infrared (FTIR) microspectroscopy measurements of fingermarks exposed to elevated temperatures, that increases in the OH stretch band may be due in part to the oxidation of unsaturated triglycerides, in addition to other lipids [52]. However, hydroperoxide formation is favoured in polyunsaturated fatty acids (the high 'drying' rate of linseed oil is due to its high content of linolenic acid (FA 18:3)) [53, 54]. In human sebum, monounsaturated and saturated fatty acids are predominant, with polyunsaturated fatty acids (primarily sebaleic acid and linoleic acid) being present in trace amounts [55]. Therefore, fatty acid hydroperoxides are unlikely to be major fingermark degradation products [52]. The peroxidation rate of triglycerides is reported to be significantly lower relative to that of other skin surface lipids such as squalene and cholesterol (see sections 7.3.2 and 7.3.3) [49]. Zhou *et al*. noted that triolein did not undergo degradation *in vitro* in the absence of ozone [56]. This is consistent with the fact that most abundant unsaturated fatty acids in human skin surface lipids are monounsaturated, and so will be more readily oxidised by ozone [46, 56].

It is accepted that atmospheric ozone reacts with a double bond to ultimately produce an ozonide as described by the Criegee mechanism (Figure 4) [57, 58]. In brief, ozone attacks the double bond to form a primary ozonide (1,2,3-trioxolane), which almost immediately decomposes to produce a carbonyl and a zwitterion known as a Criegee intermediate. In the absence of a protic solvent (such as alcohols or water), these two intermediates recombine to form a more stable secondary ozonide (1,2,4-trioxolane). Complete ozonolysis of a polyunsaturated species is progressive, with monoozonides being the first oxidation products formed, before eventual total conversion to the fully oxidised compound [24, 56, 58].

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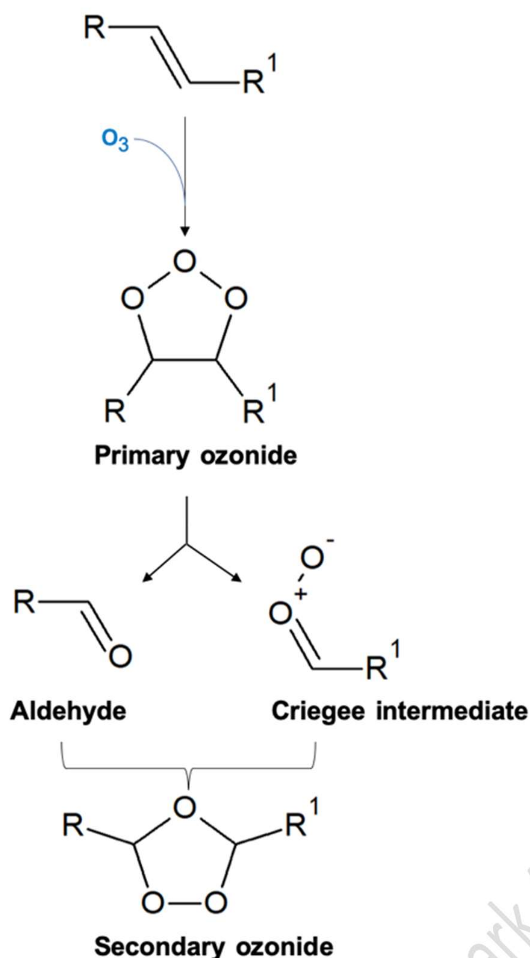

Figure 4: Criegee mechanism of ozonolysis

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Unsurprisingly, the identified degradation processes of fingermark glycerides are largely similar to the free fatty acids. Unsaturated sebaceous triglycerides can contain up to 9 double bonds, providing multiple target sites for oxidative processes [59-61]. While ozonolysis products of diglycerides have not been observed in fingermark samples, it has been demonstrated using standard solutions that they also undergo the same reaction [43]. Pleik *et al*. first identified ozonolysis as a major aging process for unsaturated fingermark triglycerides under ambient atmospheric conditions through monitoring the degradation of a single triglyceride (TG 48:1) to its ozonide [24]. Frick *et al*. were able to identify several mono- and diozonides of several triglycerides in fingermarks collected from a small sample population, using ultra performance liquid chromatography-ion mobility spectroscopy-quadrupole time-of-flight mass spectrometry (UPLC-IMS-QToF-MS^E) [62]. Additionally, they were able to tentatively identify other ozonolysis products resulting from the cleavage of the primary triglyceride ozonides to form aldehyde and carboxylic acid derivatives (summarised in Figure 5).

In the presence of protic solvents, the Criegee intermediates can react with these rather than recombining with the carbonyl intermediate [46, 57, 58, 63]. With increasing numbers of double bonds, there are therefore more instances where an unsaturated lipid may undergo side reactions before secondary ozonide formation is completed. Lower molecular weight degradation products are formed from the decomposition products of the primary ozonide through reactions with water [64-67]. Aldehyde and carboxylic acid derivatives of fingermark triglycerides were identified in addition to

their ozonides via UPLC-IMS-QToF-MS^E [62]. Such structures were also reported by Hinners *et al*. via matrix-assisted laser desorption/ionisation mass spectrometry (MALDI-MS), but were attributed to in-source decomposition of secondary ozonides rather than fingermark aging [43]. Sun *et al*. reported that similar decomposition products were formed as minor products of ozonolysis of a triolein standard [58]. Zhou *et al*. observed that ozonide yields were much lower when ozonolysis was performed at high humidity (50 % RH) compared to low humidity conditions [56], which would be an important factor to consider in the age estimation of fingermarks based on the oxidation of unsaturated lipids.

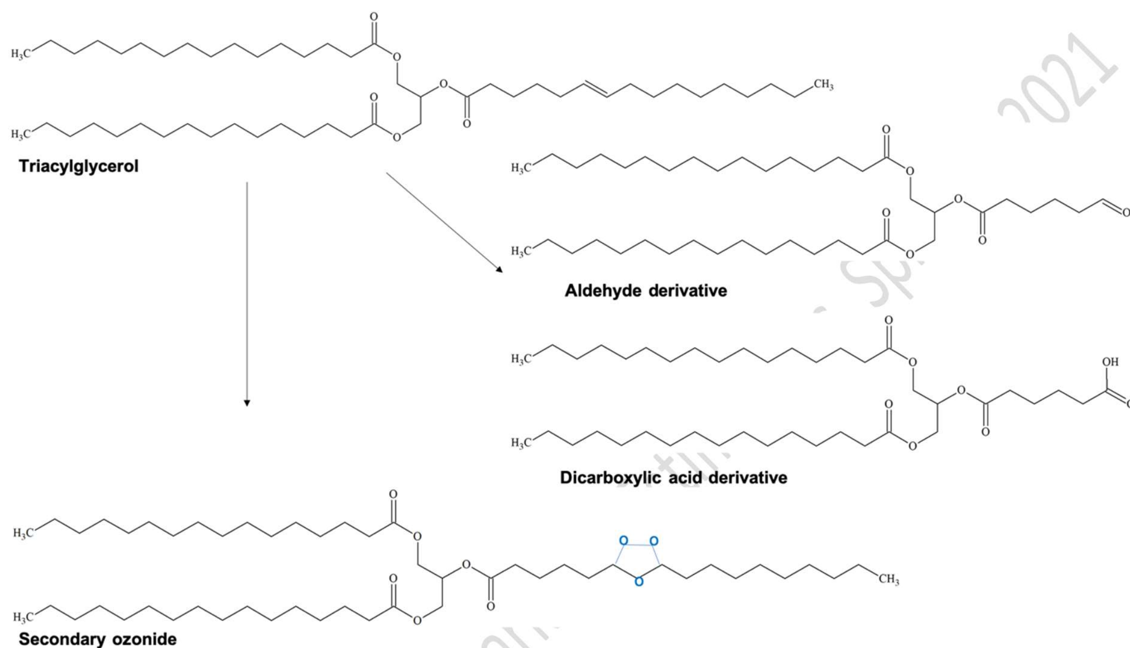

Figure 5: Example molecular structures of degradation products of triglycerides

In summary, with increasing fingermark age, the lipid fraction becomes predominantly saturated, as the unsaturated glycerides and free fatty acids are rapidly depleted by ozonolysis [24, 43, 62]. This change in lipid composition occurs soon after deposition, and has been reported to take place within the first few days following deposition on non-porous substrates [24, 43]. The resulting aged residue is therefore more viscous, consistent with the 'waxy' residue described by Mong *et al*. [16]. Oxidised fingermark residue would therefore be less compatible with detection methods such as lipophilic dyes (which partition into lipid residue), powdering (which relies upon mechanical adhesion to the fingermark) and methods which target the double bond functional group, such as iodine fuming. Due to the high triglyceride content of human sebum, and the high number of unsaturated constituents, this degradation process has potential as a means to estimate the age of a latent fingermark [24, 43].

7.3.2 Squalene

Due to its abundance in human sebum, and its high degree of unsaturation, squalene is considered to be the most significant skin surface lipid in terms of chemical reactivity, acting as a major scavenger for both singlet oxygen and ozone. Once exposed to the environment of the skin surface, squalene is exposed to numerous other stressors, including UV radiation and skin flora, culminating in the formation of a wide variety of volatile degradation products and intermediates [46, 49]. The oxidation

of squalene also occurs in latent fingermarks; the rapid degradation of this compound is one of the most prevalent chemical changes reported in investigations into fingermark aging [14-16, 44, 68]. The longevity of squalene in latent fingermarks has been reported in the range of seven days to over a month, depending on factors such as substrate and storage conditions (discussed in greater detail in section 7.4). No further studies on squalene have been reported covering longer aging periods and it is thus unknown how long squalene can be detected in fingermark residue after deposition.

Through *in vitro* experiments, numerous photooxidation products of squalene, namely hydroperoxides and squalene epoxide, have been identified [14, 47]. These oxidation products of squalene are produced via reactions with singlet oxygen and appear to be short-lived both *in vitro* and in fingermarks. On the skin surface and in fingermark residue, singlet oxygen is generated by UVA exposure of endogenous photosensitisers. A notable example is coproporphyrin, which is produced by skin flora [69], though it is unknown how long these compounds would last in latent fingermarks. However, squalene peroxidation can also occur in the absence of a photosensitiser when exposed to light, albeit at a slower rate [14]. A study conducted by the Savannah River Technical Centre investigated degradation products of fingermark lipids as potential detection targets [70, 71], utilising a mixture of lipid standards [45, 70]. The main degradation products were identified as hydroperoxides of unsaturated lipids, particularly squalene [45, 72]. While Mountfort *et al*. were able to identify more highly substituted squalene hydroperoxides from oxidation of a standard solution after 1 day, only the monohydroperoxides (SQ-[OOH]) were detected by Mountfort *et al*. and Dorakumbura *et al.* in fingermark samples up to 7 days old [14, 73]. Furthermore, it was observed in both studies that the formation of squalene oxidation products is very rapid, as SQ-[OOH] and SQ-epoxide can also be detected in freshly deposited fingermarks.

Squalene is also progressively degraded via ozonolysis, yielding a plethora of short-chain degradation products in both the gas and condensed phases [46, 74]. Ozonolysis products which themselves contain double bonds continue to oxidise further to secondary and tertiary degradation products, namely volatile ketones and aldehydes [46, 75]. Four primary squalene ozonolysis products 6,10-dimethyl-5,9-undecadien-2-one (geranyl acetone), 5,9,13-trimethyl-tetradeca-4,8,12-triene-al (TTT), 4,8,13,17,21-tetra-methyl-octadeca-4,8,12,16,20-pentaene-al (TOP) and 4,9,13,17-tetramethyl-octadeca-4,8,12,16-tetraeneal (TOT)) have been identified via GC-MS in latent fingermarks extracted 5 – 10 minutes following deposition [76]. These results are unsurprising given the reactivity of squalene, and that ozonolysis would also take place on the donors' skin prior to sample deposition. More recently, Dorakumbura *et al*. identified SQ-[OOH], SQ-epoxide and TOT in fingermarks up to 7 days old using ultrahigh-performance liquid chromatography-high resolution accurate mass Orbitrap™ mass spectrometry (UHPLC-HRAM Orbitrap™ MS), confirming that several squalene oxidation pathways occur simultaneously during aging [73]. Figure 6 provides a summary of squalene oxidation products that have been identified in latent fingermarks.

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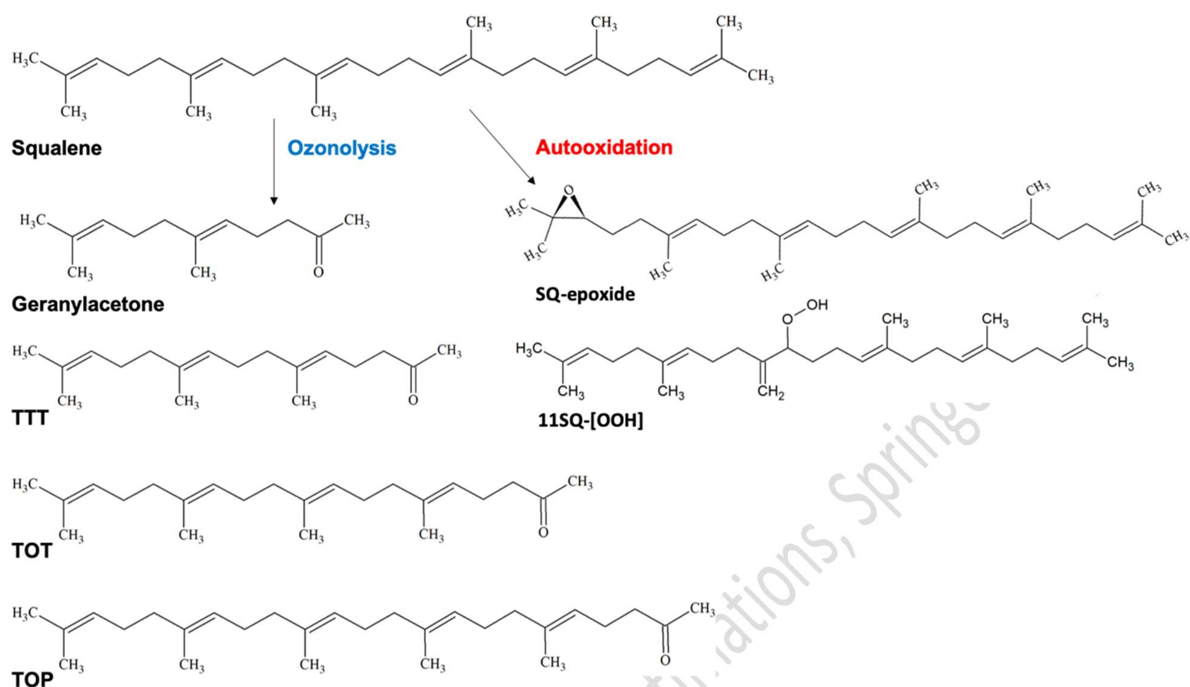

Figure 6: Molecular structures of oxidation products of squalene identified in fingermarks

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7.3.3 Cholesterol and sterol esters

Cholesterol and its esters comprise a very minor fraction of human sebum (approximately 5 %), and their aging in fingermark residue has not been investigated in as much detail as the lipids described above. Weyermann *et al*. determined that cholesterol appeared to be a relatively stable fingermark component, compared to the more readily oxidised squalene [44]. Being unsaturated, cholesterol and sterol esters (particularly those esterified to unsaturated fatty acids) are subject to similar oxidation processes to those described in previous sections of this chapter. Oxidation products of cholesterol in fingermark samples were tentatively identified by Dorakumbura *et al*. using UHPLC-HRAM Orbitrap™ MS, but characterisation was not possible as isobaric compounds were unable to be distinguished [73].

Cholesterol is oxidised by both singlet oxygen and ozone to produce a series of hydroperoxycholesterols (ChOOH) (including 5α-, 6α-, 6β-, 7α- and 7β-ChOOH), and 3β-hydroxy-5-oxo-5,6-secocholestan-6-al (together with its aldolization product 3β-hydroxy-5β-hydroxy-B-norcholestane-6β-carboxaldehyde), respectively [77, 78]. Picardo *et al.* observed that both free and esterified cholesterol were degraded by UV exposure *in vitro* and *in vivo* on human skin [49]. Similarly, Yamazaki *et al*. reported that higher amounts of 7α- and 7β-ChOOH of both free and esterified cholesterol were recovered on skin following sunlight exposure (Figure 7), indicating photooxidation as a major pathway for cholesterol degradation [78]. Thus, it seems reasonable to envisage that these degradation processes could also take place in fingermark residue. The research on this topic is currently lacking, and further studies on this aspect of fingermark aging are required.

7α-ChOOH 7β -ChOOH

Figure 7: Molecular structures of cholesterol 7α- and 7β-hydroperoxides

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7.3.4 Wax esters

Wax esters have been reported as components of both fresh and aged fingermark residue [70]. However, there is little information currently available in the literature concerning the degradation products of these compounds due to age or other influence factors. Mong *et al*. reported that unsaturated wax esters appeared to undergo degradation, but at a slower rate compared to other unsaturated components such as fatty acids and squalene [16]. Girod *et al*. studied the aging of targeted lipid compounds, including wax esters, based on peak areas resulting from GC separation [25]. Decreases were observed in the peak areas of the target lipids over time, indicating the occurrence of degradation processes, but specific mechanisms were not proposed. Given that a number of wax ester species are unsaturated, it follows that they would behave similarly to other unsaturated sebaceous components. For example, wax esters appear to peroxidise to a small extent under UV radiation, but to a lesser extent to more reactive species such as squalene [49].

Recent investigations using wax ester standards shed more light on processes likely to occur in fingermarks. It has been demonstrated that as with the unsaturated lipids described above, unsaturated wax esters undergo ozonolysis [43, 79]. However, saturated wax esters do not seem to react in any way [52]. These preliminary results show that the question of how wax esters degrade in fingermark residue still requires further investigation.

7.4 Factors affecting chemical degradation of fingermark components

As described by Wertheim, a reliable age estimation method would ideally be based on a reaction that occurs mainly as a function of time, with minimal influence from external factors [9]. However, many different influence factors have been reported in the literature as having a significant impact on the initial and aged composition of latent fingermarks [15, 16, 25, 35, 68, 80, 81]. These factors encompass a number of variables that affect fingermark composition before (i.e. donor influence and presence of exogenous substances on the fingertips), during (e.g. substrate, time of contact, deposition pressure) and after deposition (interaction of residue with substrate and environment).

For both fingermark detection and construction of aging models, it must be borne in mind that different factors will affect the degradation of certain compounds to a greater extent than others [82]. As an example, the performance of Oil red O (ORO) for the visualization of latent fingermarks is

generally considered to be inferior to that of physical developer on specimens more than 4 weeks old, due to oxidation of the neutral lipids that ORO targets, as well as their diffusion into porous substrates [41]. Physical developer, on the other hand, continues to be successful on fingermarks up to several decades old [32], presumably as the targets of this detection method remain fairly stable. However, Beaudoin reported the successful application of ORO to develop a fingermark on a paper substrate recovered by police 21 years prior [83].

The first part of this section will discuss the particular impact of the initial composition (t=0) on the aging of fingermarks, and the factors that contribute to its variation across individuals over time. The remaining discussion will detail some of the main factors influencing the known chemical changes in fingermark composition that occur over time (t>0) (Figure 8).

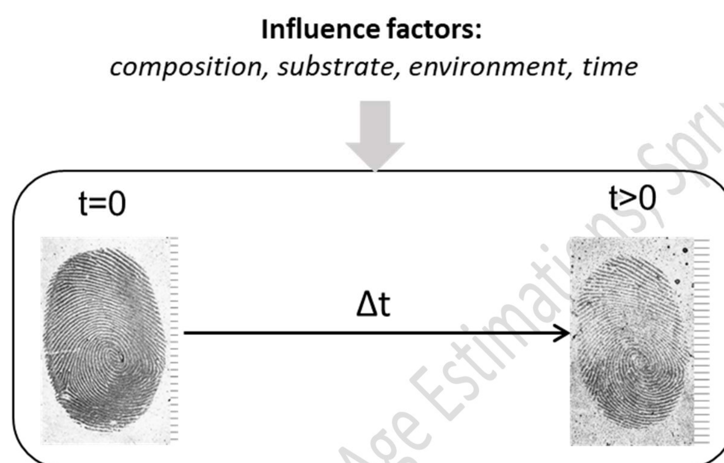

Figure 8: Schematic representation of factors affecting fingermark composition over time, from the initial moment of deposition (t=0) to the aged mark at the time of the crime scene investigation (t>0).

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7.4.1 Initial chemical composition (t=0)

Latent fingermark residue can vary considerably in qualitative and quantitative composition, depending upon factors such as, but not limited to, an individual's age, the time since they last washed their hands, the substances they recently handled (e.g. sebum and skin products from touching the face or hair) or the transfer conditions applied (e.g. pressure or time of contact) when depositing he fingermark [25, 76, 80, 84]. The wide array of combinations has a subsequent effect upon the way a fingermark ages, in regard to the limits of detection of certain components and/or their degradation products, but also the interactions between certain fingermark components can impact longevity. Latent fingermark residue is an emulsion of water-soluble and water-insoluble components [85], and so the presence of both fractions can be considered as a matrix in which volatile and/or water-soluble compounds are trapped within a matrix of non-volatile lipids and proteins [86]. However, this complex matrix presents a significant challenge to the study of fingermark aging, as the chemical and physical interactions of all of these different components will have an impact on individual degradation rates, compared to those of pure compounds.

Interactions between fingermark components

As an example of interactions between fingermark components, squalene is considered to have a protective role in skin surface chemistry, by being preferentially oxidised in lieu of other unsaturated skin surface lipids upon exposure to UV radiation [87]. As squalene is present in unusually high concentrations in sebum, the onset of degradation of unsaturated fatty acids, for example, could be delayed in fingermark residue until its squalene content is sufficiently depleted. Furthermore, Mountfort *et al*. observed that the photooxidation of squalene was more rapid in fingermarks than *in vitro* and attributed this to the higher concentration of squalene in standard solutions. However, the fingermark degradation was compared to a squalene standard that had been oxidised in the absence of a photosensitiser. As stated in 7.3.2, the skin surface contains several endogenous photosensitisers including coproporphyrin and riboflavin. Thus, these observations could also be due to the influence of photosensitisers on squalene oxidation.

Another interesting point to highlight is that the bulk residue may physically protect some components from degradation or evaporation, slowing the rate of aging mechanisms compared to standard compounds stored under the same conditions [24]. For example, individual lipid standards deposited onto a surface exhibit faster reaction rates compared to analogous lipids within fingermark samples [24, 73]. Moreover, Kim *et al*. observed that concentrations of squalene and cholesterol standards decreased significantly at 60 °C, whereas in fingermark samples, these compounds showed greater stability at the same temperature [82]. Johnston and Rogers proposed that the chemical species that comprise human sebum might interact in such a way as to influence each other's degradation rates [88]. Possible interactions in fingermark residue include cholesterol with triglycerides and free fatty acids [89], and squalene and unsaturated fatty acids [90]. Johnston and Rogers investigated the influence of major sebaceous lipids on degradation of the bulk residue using a series of 'fingermark analogues', mixtures of representative fingermark components that were each missing a component such as triglycerides or serine [88]. Examination of the analogues using FTIR microspectroscopy indicated that squalene and cholesterol play a role in interactions with other fingermark lipids and suggested that this could impact aging processes.

Donor variation

The inter-individual variability (differences between persons) of both fresh and aged fingermark composition is clearly illustrated by the differences in persistence between fingermarks deposited by adults and children. There have been several case examples where a child was known from eyewitness testimony to have been in physical contact with a surface (such as the interior of a car), but upon forensic examination, only the fingermarks of the adult suspect could be detected [81, 91]. Subsequently, this phenomenon become the subject of a series of investigations. Using GC-MS, Buchanan *et al*. found that the fingermarks of prepubescent children contained far fewer non-volatile lipids, such as wax esters, which accounted for the observation that children's fingermarks could 'disappear' within hours of deposition, while under the same conditions, adults' fingermarks could still be detected after several weeks [81, 91]. Similar results were obtained by Mong *et al*. [16]. The difference in composition can be attributed to the onset of adrenarche, which occurs at approximately 7 – 10 years of age, during which the production of androgens stimulates increased sebum production (before this stage of development, the sebaceous glands are largely inactive) [92]. Due to the inter-variability already present in fresh fingermarks, samples from adults and children will age differently, such that they can be clearly distinguished several weeks after deposition [17].

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Other sources of inter-individual variability in fingermark composition have been attributed to factors such as the biological sex of the donor and ethnicity, however the specific impacts of such characteristics have never been determined in detail [80]. It has been shown that fingermark composition can vary to such an extent that individuals can be classified as poor or rich lipid donors [76]. Furthermore, the intra-individual variability of fingermark residue (variability among fingermarks from the same individual deposited at different moments may also influence aging. Changes in lifestyle factors such as diet, certain metabolic disorders, consumption of medication or drugs can affect the initial composition through qualitative or quantitative variation [22, 93]. As an example, fingermarks deposited by an individual who used acne cream were observed to contain significantly higher quantities of lipids when its use was ceased [22]. It has also been demonstrated that handwashing can influence the initial relative water content of fingermarks [29], through removal of the secretions and contaminants present on the fingertips. However, this effect may not be long-lived, as eccrine sweat is continuously secreted onto the fingertips. Lewis *et al*. demonstrated that when deposited 5 minutes after hand washing, fingermarks already contained enough eccrine components to be successfully developed using cyanoacrylate [38]

In summary, inter- and intra-individual variation presents a significant complicating factor into understanding fingermark composition and its degradation processes [27, 68, 85]. Girod *et al*. have suggested that inter-individual variation may be impossible to overcome, such that a means to estimate fingermark age necessitates the construction of an aging model for each individual [94].

Transfer conditions

While intra-variability has been identified as one of the main factors influencing the initial fingermark composition, conditions surrounding the transfer of material from the fingertip to a surface also have an impact. For example, the effects of deposition pressure have been investigated in the transfer of fingermarks onto a porous substrate [25]. A greater mass of residue was transferred when fingermarks were deposited at a pressure of 1000 g compared to 100 g, though intra-donor variability of the normalised data was greater than the variability induced by differences in pressure. Subsequently, the aging of squalene contained in the fingermark deposited at 100 g pressure could no longer be monitored after 5 days following deposition using GC-MS, as the remaining quantities fell below the limits of detection (conversely, squalene aging could be observed up to 18 days in samples deposited at 1000 g). Fieldhouse *et al*. reported that increased deposition pressures created fingermarks with larger surface areas, and hence a greater amount of deposited residue. [29, 38, 84]. Further studies are required to determine the impact of other transfer conditions, such as contact time, and the temperature of the substrate.

7.4.2. Substrate

The characteristics of the substrate on which a fingermark is deposited can affect the initial composition and its aging. In fact, a porous substrate such as paper will absorb a greater quantity of residue from the fingertip ridge skin than a non-porous surface such as metal or glass [44]. Fingermark components such as amino acids will penetrate into such substrates, with the extent of residue absorption depending on factors such as the smoothness and porosity of the paper [95]. The porosity of substrates enables fingermark detection long after deposition, for example with techniques such as amino acid-sensitive reagents and physical developer, as shown in a very recent study [32]. Similarly, the ‘fixing’ of lipid-rich fingermarks on certain polymer substrates such as powder-coated aluminium PVC or painted surfaces has also been attributed to the absorption of fingermark residue into porous and semi-porous substrates [12]. On the contrary, smooth, non-porous substrates are less

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absorbent, and so may leave deposited residue vulnerable to chemical degradation or mechanical abrasion. Wargacki *et al*. observed that eccrine fingermarks appeared to degrade due to physical removal of brittle salt residue from eccrine fingermarks by air currents, in tandem with chemical degradation [38]. Furthermore, it has also been observed that squalene and cholesterol degrade faster on a non-porous substrate [44].

Substrate properties other than porosity will also impact fingermark aging, due to the interactions of certain materials with fingermark constituents. For example, it has been observed that the photodegradation of lactic acid is faster on galvanised steel than Teflon, due to the iron content of the former substrate [34]. Concerning metal substrates, inorganic salts originating from eccrine sweat react with metals such as aluminium and brass, resulting in a durable image of the fingermark pattern via corrosion of the substrate [96]. This process occurs at temperatures at up to 600 °C, preserving the ridge pattern even under circumstances that would destroy the organic fingermark constituents (e.g. arson and ballistics). The resulting quality of the fingermark pattern is affected by both the type of the metal substrate and the concentration of salt in the latent residue (dependent on donor factors) [97]. A study by Girod *et al*. found that fingermark samples deposited on glass and aluminium stored in the dark and analysed with FTIR microspectroscopy could be differentiated by substrate, rather than by age [20]. While this was not observed in samples that had been stored in the light, it is possible that the acceleration of aging processes brought on by light exposure masked any substrate effects.

7.4.3 Environment

Light

Exposure to direct natural light, particularly UV radiation, has been linked to the increased degradation rate of several lipid components, particularly squalene [15, 19, 68, 73]. As described in 7.3.2, UVA exposure leads to the increased formation of singlet oxygen, and therefore enhanced fingermark peroxidation. Thus, even fingermarks stored indoors behind a window can exhibit UV-induced degradation, as ordinary glass transmits most UVA radiation. Conversely, it has been suggested that exposure to UV light might preserve certain fingermark components by destroying microbial activity [98]. However, several analytical investigations have concluded the degradation rate of sebaceous components including squalene, cholesterol and free fatty acids is accelerated when latent fingermarks are exposed to light over a period of days to weeks [15, 19, 24, 45].

It is interesting to note that, even when fingermarks are stored in the dark, the degradation of some unsaturated lipid compounds (particularly squalene) may still be observed [15, 19, 44]. The quantity of low molecular weight saturated acids has been reported to increase over time in fingermark samples stored in the dark [16]. These components could originate from the oxidation of fatty acids, glycerides and squalene as described in 7.3.1 and 7.3.2, and hence such degradation processes would occur in fingermarks regardless of light exposure.

Information is rather limited in the literature concerning the effects of light on the degradation of eccrine components. As described in 7.2.3, lactic acid degrades to pyruvate when exposed to artificial sunlight [34]. This is consistent with observations that fingermarks exposed to UV light exhibit poorer ridge quality upon cyanoacrylate fuming [38], and that pyruvate is a less effective initiator of superglue polymerisation than sodium lactate [99]. This was attributed to the lower pH value of the pyruvate standard. Other fingermark eccrine components, such as amino acids and proteins, appear to not be affected by photo degradative processes [19, 34]. Conversely, Girod *et al*. observed that IR peaks relating to esters and eccrine constituents decreased faster when fingermark samples were exposed

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to artificial and natural light (through a window) [20]. Further research on this topic should be conducted in order to obtain definitive results.

Air flow, water and ambient humidity

The oxidation of fingermark lipids occurs rapidly, regardless of temperature and exposure to natural or artificial light [15, 52]. Ozone in particular is a highly reactive species, and can be rapidly depleted in small, constricted spaces, such as drawers, if there is no circulation of air from ozone-rich sources to replenish ozone levels. As a result, lipid ozonolysis may be significantly slower [24]. Furthermore, human presence in an indoors setting has a significant effect on ozone concentration, due to the presence of sebaceous lipids on skin, hair and clothing, as well as handled surfaces, and the reactivity of surface lipids within the respiratory system [46, 65]. Thus, if fingermarks are deposited in a relatively contained environment with many people present (such as a shared office or home), the ozone content of the air will decrease, and the ozonolysis rate of fingermark residue will probably be slower compared to an outdoors setting [46, 74].

It should be noted that aging studies, particularly comparisons between degradation rates of fingermark compounds with and without exposure to light, normally involve wrapping or otherwise containing samples in order to protect them from natural and artificial light [15, 16, 24]. This may have the unintended consequence of also impeding degradation processes by restricting both the initial availability of ozone and other reactive gases and their replenishment by airflow. Both opaque and transparent containers have been demonstrated to significantly reduce the rate of ozonolysis in fingermark lipids compared to when samples were exposed to ambient air for the same amount of time [24, 43].

In instances where objects are submerged, it might be assumed that sebaceous lipids may be preserved, due to the lower availability of oxygen and ozone in water compared to air. However, Dorakumbura *et al*. observed that squalene degradation was increased when fingermarks were submerged and stored in covered containers compared to samples stored in dark and dry conditions [73]. The persistence of sebum-rich fingermarks is also affected by water quality. Sutton *et al.* found that fingermarks on non-porous substrates were of worse quality after immersion in water collected from natural water sources and stored in tanks, than those submerged directly in water sources (e.g. lakes or rivers) [100]. This was attributed to microbial accumulation in the tanks used to contain samples in the laboratory, which in turn degraded the fingermark lipids.

As described in 7.2.2, elevated humidity can affect fingermark composition by dissolving water-soluble components, such as amino acids and chloride, out of the residue [2]. Additionally, humid storage environments can affect the formation of lipid oxidation products, through interaction of water vapour with ozonolysis intermediates, as described in 7.3.1.

Temperature

Increased temperatures can accelerate the oxidation of fingermark lipids, which would subsequently lead to greater mass loss through evaporation of the volatile degradation products. Johnston *et al*. noted that at temperatures of 55 °C or more, peak signals corresponding to sebaceous material decreased more rapidly over a 5 hour period compared to when samples were stored at 45 °C, which was attributed to an overall decrease in sample mass and to chemical modifications of some functional groups [52]. Girod *et al.* investigated the effect of environmental temperature (15°C, 20 °C, and 25 °C) on lipid degradation and demonstrated that squalene degradation was accelerated by increased

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temperatures [25]. Similarly, Kim *et al*. reported that short-term storage (up to 8 hours) at 100 °C increased the degradation rates of both squalene and cholesterol in fingermark samples [82]. Wolstenhome *et al*. investigated the effects of increasing temperatures on fatty acid aging, reporting that oleic acid degraded at faster rates at 37°C and 60 °C, compared to 4 °C [101]. Degradation products were identified using MALDI-MS imaging as dehydrated and didehydrated oleic acid, indicating that temperature may influence the specific degradation reactions that occur, as well as degradation rates. Lower signals from the dehydrated forms of oleic acid were detected at 60 °C compared to 37 °C, indicating further decomposition of the fatty acid.

Amide groups appear to be less affected by storage temperature [52], which is consistent with studies indicating that fingermark amino acids do not decompose at temperatures below 100 °C [18, 34]. This would suggest that amino acid degradation due to temperature is not of particular concern from a forensic perspective, except for cases involving extreme environmental conditions, such as arson [18, 34]. As described in 7.2.3, some additional eccrine constituents such as urea also undergo thermally-induced degradation, while FTIR analyses have demonstrated that carboxylic acid salts (i.e. sodium lactate) may still be detected in fingermarks residue after storage at 70 °C for 72 hours [102].

Microbial activity

The free fatty acids in human skin surface lipids are derived from digestion of sebaceous triglycerides by facultative anaerobes within the secretion ducts of the sebaceous glands [103-105]. *Cutibacterium acnes* (formerly referred to as *Propionibacterium* or *Corynebacterium acnes*) has been identified as one of the main species responsible for hydrolysing triglycerides to produce a variety of di- and monoglycerides, as well as free fatty acids [106-108]. It has been proposed that given appropriate environmental conditions, such bacteria could survive on a substrate such that this or other enzymatic process would continue to modify the composition of the latent fingermark residue [23, 33]. Preferential bacterial growth in latent fingermarks has been demonstrated, under controlled conditions, as a novel visualisation method [109]. Skin flora from multiple genera may be deposited onto a surface through contact with friction ridge skin, however their subsequent longevity has not been investigated [110]. A more in-depth discussion on the potential effects of microbes on fingermark degradation is discussed in Chapter 11.

7.4.4. Time

The passage of time following deposition will also have an influence on the aging of fingermarks, and the investigated timeframe is thus an important factor to take into consideration when studying aged composition. As described in sections 7.2 and 7.3, some aging processes, such as the evaporation of water, will occur within minutes [29]. Other compounds, such as fatty acids, squalene and glycerides, will degrade more slowly over a period of several days to weeks [15, 16, 23, 24]. Squalene and cholesterol have been shown to decrease exponentially in the first few hours after deposition [44] and the remaining quantities of these compounds may fall below the limits of detection within a month, depending on other factors such as light exposure, poor lipid donors and low deposition pressures [15, 25]. Saturated lipids appear to be relatively unaffected by degradation processes [16, 52], and may persist for longer periods than have currently been explored. While few investigations have been carried out over timeframes greater than one or two months, there are a limited number of studies which indicate that some compounds, (such as amino acids [27, 32]) can still be detected years after deposition. The fact that detection methods such as powdering, ORO or physical developer may still

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be effective on years-old fingermarks [12, 26, 32, 83] indicates the presence of target compounds in the aged latent residue. It is, however, currently unclear if target compounds which comprise the initial composition can still persist in the aged latent residue, or whether some degradation products may also act as targets for detection methods. Further, long-term studies would be required to determine such processes and whether degradation products may act as detection or aging targets.

7.5 Considerations for aging studies

As stated in the introduction of this chapter, research concerning the aging processes of fingermarks based on chemical degradation serves several purposes. It is essential to acquire fundamental knowledge of the composition of fingermarks discovered at crime scenes (i.e. at time $t>0$) to target appropriate compounds for detection. Thus, such knowledge will help to understand, develop or improve detection techniques. While a detection method should ideally work on all fingermarks, regardless of age, it is theoretically possible that a method that targets compounds more common to aged fingermarks could be employed in instances where the approximate age of a fingermark is known, and thereby 'filter out' other fingermarks less relevant to the investigation. The use of detection techniques for such purposes is, however, rather difficult to implement in practice. For the development of methods for age estimation, one proposed approach to place fingermarks in time is to measure its chemical degradation. For both lines of enquiry (i.e. detection and age estimation), it is necessary to consider fingermarks as complex biological matrices. While experiments with standard solutions can be performed to confirm observations noted in fingermark samples [14, 18, 23, 24, 52], these cannot be reliably used to infer fingermark aging processes (particularly degradation rates) on their own. To ensure that such investigations are relevant in practice, some parameters should be observed as discussed below.

First of all, it must be noted that many aging studies, particularly those which focus upon lipid constituents, utilise groomed or charged samples, which are typically prepared by having fingermark donors rub their fingertips on their nose and forehead, where sebaceous glands are found in greatest density [15, 16, 25, 43, 68]. While this ensures that sebaceous compounds are present at detectable levels, it also risks misrepresenting the composition and degradation processes of latent fingermarks recovered in criminal investigations [80]. As per recommendations from the International Fingerprint Research Group [111], research needs to move away from groomed fingermarks as the sole type of sample investigated. Several studies in more recent years acknowledge the importance of investigating 'natural' fingermarks deposited without prior preparative steps on the part of the donor, as well as eccrine fingermarks prepared by cleaning the hands of any sebum and exogenous materials (using water and soap, or solvent) [37, 43, 73].

Because of high intra- and inter-individual variability in initial fingermark composition, several approaches have been reported in order to obtain more reproducible samples, particularly in studies utilising destructive methods such as GC- and LC-MS. A homogenisation step, consisting of rubbing the fingertips together before depositing fingermarks, is sometimes employed in order to minimise intra-individual variation [15, 62, 112]. The use of synthetic mixtures intended to mimic fingermark composition has also been proposed to minimise sample variation [113]. While such approaches may be used to gain initial insight into fingermark aging, the use of more realistic samples would be required in subsequent stages of research, particularly when developing methods aimed to be used in practice. As significant variability of fingermark composition has been observed by many researchers, it is important to understand the extent of this variation by using more realistic, natural (i.e. 'non-groomed') fingermarks. This will enable the identification of the (groups of) components

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present in most or all fingermarks, whatever their age, as these 'common factors' will serve as optimal targets for the development of more broadly applicable detection and/or age estimation approaches.

Substrates should also be chosen in accordance with the purpose of the conducted study. Clean substrates that are most compatible with the analytical technique(s) employed are again useful to gain fundamental knowledge about fingermark composition and aging in the initial stages of research. Fingermark studies often utilise brand new, thoroughly cleaned laboratory materials such as filter paper or microscope slides [15, 21, 43, 62, 76]. This is necessary to minimise complications such as contamination and high signal-to-noise ratios, as well as for more prosaic reasons such as ease of handling by the researcher, or limitations of certain analytical instruments. However, for validation and implementation of age estimation approaches, eventually the methodology must comply with substrates which more closely resemble those encountered at crime scenes (e.g. white copy paper rather than filter paper or patterned aluminium cans rather than pre-cleaned sheets).

In the first stages of research, it is vital to know the conditions of the sample storage environment to evaluate their specific influence on aging processes and the resulting aged fingermark composition [113]. At a minimum, monitoring of storage conditions should be conducted. If these are not directly controlled, the absence of information of aging conditions in experiments can make it difficult to compare results, as well as infer variables that may cause differences in results, in a rational and informed manner. In particular, conditions such as the type and duration of light exposure, temperature and relative humidity should be disclosed. However, uncontrolled (or realistic) conditions should also be explored in the final stages of the development of age estimation approaches, as these might have a non-negligible impact on the targeted chemical degradation process(es) (as explained in 7.3).

Crime scene investigations rarely commence within the first few hours after fingermark deposition and thus, the timeframe of aging experiments should be designed appropriately [111]. For example, if the goal is to monitor certain target compounds for the purpose of fundamental data, it may be appropriate to conduct the study for as long as the target compounds can be detected, weeks to months for sebaceous compounds and possibly several years for some eccrine components, starting from immediately after sample deposition. However, for the development of an age estimation methodology, more relevant time frames should be selected with consideration to the reality of forensic investigations. The ability to differentiate between fingermarks that are a few days old, and a few weeks or few months old would already represent a significant gain to forensic practice [26]. Thus, analyses should be conducted up to at least 3 – 4 months (if target compounds are still detectable). Sebaceous lipids would be appropriate targets for such timeframes. If the focus is set on longer timeframes of up to several years, eccrine compounds may be preferable analytes.

The choice of the analytical technique(s) will also be dependent on the pursued aims. In a fundamental research context, high-cost, state-of-the-art instruments may be preferred when available for their advantages such as improved sensitivity and high mass resolution. Such approaches might also be applied in high profile cases, but complete validation of the methodology in realistic conditions should not be underestimated. However, for the development of an age estimation model intended for eventual routine practical use, analytical techniques more readily available to forensic laboratories should be prioritised. Moreover, non-destructive approaches (e.g. FTIR on non-porous substrates or headspace extraction approaches) that can be applied in sequence with detection techniques present advantages over methods that require solvent extraction, such as GC- or LC-MS. Following data acquisition, reliable data processing is of uttermost importance. Pre-processing techniques may be used to increase reproducibility of selected aging parameters and chemometrics should be considered to enable the evaluation of univariate and multivariate modelling. However, it should be stressed that

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while data processing can be employed to reduce variability, it will never be entirely controlled, as a forensic trace is by its very nature produced in an uncontrolled manner, and is not always representative of its source [114].

7.6 Conclusions

Fingermarks are complex biological matrices whose initial composition differs from person to person, as well as over time from a single person, and is influenced by many factors that come into play before, during and after deposition. The identification and understanding of aging processes are therefore a considerable challenge. Indeed, fingermarks are comprised of a diverse range of components mainly originating from the skin, but also external contaminants such as cosmetics, foods and other handled substances. Several of these components, depending on the timeframe and reproducibility of their aging processes, represent potential targets for fingermark detection or age estimation.

In order to respond to the practice-oriented needs expressed by the forensic community, a detailed understanding of the chemical processes involved in latent fingermark degradation is essential. While some early investigations have inferred chemical degradation through the poor (or good) performance of certain detection methods with increasing sample age, more knowledge of the specific mechanisms involved is needed to truly understand and improve current detection capabilities and to reliably place latent fingermarks in time. While there is some information already available concerning the degradation mechanisms of some components as reported in this chapter, many have yet to be fully elucidated. Furthermore, investigations into chemical degradation of fingermark components in the context of the latent residue are required, which can produce results that diverge from more simple *in vitro* experiments. In particular, fundamental information is needed on how the initial composition, the substrate and the environment to which the latent residue is exposed interact to influence the nature and rates of the degradation mechanisms that occur between deposition and detection.

To date, the sebaceous secretions have been the main focus of aging studies, presumably because their chemical modification is known to occur in a relatively short time frame (hours to months). The degradation of compounds such as squalene, cholesterol, fatty acids and glycerides have been studied as a function of different donors (e.g. poor to good lipid donors), on different substrates (e.g. paper, glass and aluminium) and under different storage conditions (e.g. light exposure, ambient humidity and temperature). Many investigations indicate significant variability that may represent an insurmountable issue in the development of age estimation approaches. Currently, the implementation of an age estimation methodology applicable to all fingermarks seems unrealistic. It has been suggested that in practice, samples from the person who left a questioned fingermark (provided that an identification is possible) would need to be used in order to build an age estimation model that would then only be valid for a particular individual and case conditions [26]. Further research needs to be conducted, particularly concerning eccrine compounds, and other components that remain relatively overlooked, and might provide interesting aging parameters over longer timeframes. The possibility of utilising other, complementary methods (such as optical or physical characterisation, as well as detection techniques) in conjunction with chemical characterisation to better understand aging processes might also be considered as a complex, but promising approach to tackle the issue of estimating fingermark age.

While future research could focus on identifying degradation processes that are less impacted by the factors discussed in this chapter, the variability of fingermark properties (chemical and physical) over time will never be completely overcome and thus, research efforts need to coordinate and focus on

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the practical forensic context, rather than only on the technological aspects. Combined multivariate approaches might be more suited to better deal with this complexity, as different aging parameters will be influenced differently by composition, substrate, environment and time. Thus, further research on the chemical composition of natural fingermarks, to characterise degradation processes and factors influencing composition at the time of deposition, should be a primary aspect of future endeavours.

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