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Advanced Fingerprint Analysis Project Fingerprint Constituents

G. M. Mong
C. E. Petersen
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September 1999

Prepared for the Assistant Secretary of Defense,
Office of Special Technology, Technical Support
Working Group under a Related Services Agreement
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DISCLAIMER

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SUMMARY

The work described in this report was focused on generating fundamental data on fingerprint components which will be used to develop advanced forensic techniques to enhance fluorescent detection, and visualization of latent fingerprints. Chemical components of sweat gland secretions are well documented in the medical literature and many chemical techniques are available to develop latent prints, but there have been no systematic forensic studies of fingerprint sweat components or of the chemical and physical changes these substances undergo over time.

In this study, seventy-nine samples were collected from very young children, adolescent, and adult subjects in an effort to gather information which would be representative of the general population. A protocol for this collection was developed which allowed for fingerprint transfers, aging, and analysis. Only volatile components of fingerprint residue or those which could be converted to methyl esters through derivatization with diazomethane were studied. The resulting data indicated that the principle volatile components under 500 daltons are comprised of fatty acids, steroid precursors, and wax esters. Aged samples show that squalene, oleic, and palmitoleic acid undergo significant degradation after a 60 day exposure to air, with the total amount of material extracted decreasing over time, possibly degrading to smaller molecules. Thus, with aging, various degradation processes serve to shorten and oxidize components in fingerprint residue possessing unsaturated moieties in their structure. As a result, chemical functional groups which could possibly be used for fluorescent tagging, are eliminated. A significant observation was that the inherent inhomogeneity in fingerprint samples made quantitative comparisons (with respect to time) of individual components difficult. Considerable variation exists between samples obtained for these aging studies. While most adult prints yield components indicative of sebaceous secretions, the very young afford mostly aqueous saline for the print image. Irregular yet interesting results are observed in children around the age of maturation. A few samples from this age group showed cholesterol as the

major component, far exceeding the concentration of all other components. This phenomenon is very fascinating and should be subject to further investigation.

In an effort to gain a better understanding of the processes underlying current latent print development techniques, electron microscopy was used to study aged samples. Details of the aged fingerprints were developed with silver-based physical developer (PD) solution. Interpretation of the electron micrographs suggests that the PD process may in fact be driven by electrostatic forces whereby small silver particles provide a "template" that in turn attracts larger spheres of silver formed in the solution to eventually become the visible silver image of the latent fingerprint. The electron micrographs of developed fingerprint samples are included in this report.

ACKNOWLEDGEMENTS

Several people other than the authors contributed to the successful completion of the work described in this report. Robert Ramotowski of the United States Secret Service and Mark Segura of Pacific Northwest National Laboratory provided assistance in assembling a library of the known fingerprint literature and information concerning the state of the art for chemical development of latent fingerprints. Jim Young at the Environmental Molecular Sciences Laboratory (EMSL) provided electron microscopy support and micrographs. Jim Campbell, Scott Clauss, and Karen Wahl all of the Pacific Northwest National Laboratory, provided technical assistance in the completion of this report.

CONTENTS

1.0 INTRODUCTION

Successful prosecution of people who commit criminal acts requires strong evidence of the identity of the person or people involved to link them to the crime. Objects connected with virtually every type of crime, including acts of terrorism, are routinely examined for latent fingerprints. Chemical components of sweat gland secretions are well documented in the medical literature and many chemical techniques are available to develop latent prints, but there have been no systematic forensic studies of fingerprint sweat components or of the chemical and physical changes these substances undergo over time.

The goals of the advanced fingerprint project were divided into several tasks. The first task involved assembling a library of the known literature pertaining to fingerprint constituents, analysis of human skin secretions, and information concerning the state of the art for chemical development of latent fingerprints. This task was completed by a cooperative effort between Robert Ramotowski of the United States Secret Service and Mark Segura of Pacific Northwest National Laboratory. The information gathered in this phase of the project was used to explore the nature and aging characteristics of human fingerprint impressions on a neutral substrate (task 2). The emphasis of task 2 was to analyze the fatty components of the fingerprint in order to explore what types of reagents might be developed to visualize the non-aqueous components of a fingerprint image.

2.0 SAMPLING PROTOCOL

Samples of human fingerprints were collected using an internally approved protocol to protect the donor's right to privacy and safety during the collection procedure. The samples were collected blind, so that no correlation could be made between a person's print and their identity. The samples were collected from public sources not affiliated with PNNL, and thus made re-sampling impractical.

Samples were taken from volunteers by having them place their fingertips upon quartered pieces of glass fiber filter paper circles (GFA paper 4.25 cm diameter). So that a normal loading of human secretions were assured on the sample, a typical grooming motion, such as touching the face or forehead with the fingers, was encouraged prior to depositing the sample upon the

GFA paper. Prior experiments conducted in the laboratory indicated that the nature of normal fingerprints include a fair amount of sebaceous secretions, so long as the individual has not recently washed their hands, and had presumably engaged in touching of other parts of the body which have sebaceous glands. When washed hands were subjected to analysis, the only components which appeared to be present in the fingerprint samples were water soluble salts. The touching of the face is such a typical behavioral phenomenon that this was included in order to create fingerprint transfers which were laden with normal sebaceous secretions. The sampling protocol included a request that the individual donating prints affirm that they have not applied cosmetics to the skin within 6 hours of our sampling. This proved to be impractical to enforce, and often prints from adult females contained a significant amount of known cosmetic components.

The samples were collected by age grouping and sex as the only criteria provided to the analyst. The arbitrarily assigned age groupings were selected primarily to ascertain the difference in fingerprint composition, if any, between pre-pubescent children and adults. The samples collected were grouped as listed in Table 1.

TABLE 1. Categorized list of fingerprint samples.

Age Group	Males	Females
3-8 years	3	6
8-12 years	16	14
12-15 years	3	5
20-60 years	18	14

Total individuals sampled: 79

Samples were requested from the volunteers by instructing them to touch 6 sample pieces of GFA paper with the two major fingers of the hand, then to touch the paper again in reverse order with the same two fingers after a normal grooming motion. In this way, it was hoped that the samples would be somewhat homogeneous in sebaceous content, while providing a sense of security to the volunteer that the multiply touched article would be worthless as an personal identifier; the images are smeared, overlaid, and rubbed in the transfer process. The double touch employed to each sample piece was noted in our estimation of total sebaceous loading

upon each sample provided, so that we could make an estimate of the amount of component material per fingerprint when analysis was completed.

The samples were folded in aluminum foil and a numerical identifier assigned. The samples were stored in this condition (loosely packed in foil, protected from light), at room temperature (21 °C), and allowed to age under these conditions up to 60 days. The samples taken from adults were analyzed within one day of collection at 10 days, at 30 days, and at 60 days. An observation by Michelle Buchanan's group at the Oak Ridge National Laboratory was that childrens' samples (those under 12 years) were found to generally have much less sebaceous secretion than adults [1]; therefore, the protocol was modified to examine these samples at collection and at 30 days.

3.0 ANALYSIS PROTOCOL

When analysis was done, each piece of filter paper was cut in half, and a random set of three of the 12 total pieces were extracted in a serological pipette with 1:1 hexane:chloroform (1 mL) followed by acetone (1 mL) to effect a total transfer of fat soluble components to a 5mL reactivial. The samples were reduced with a dry stream of nitrogen over a 40 °C hotplate. Since some samples had a tendency to froth, a sliver of silicon carbide boiling chip was added to each sample. The samples were reduced to about 0.3 microliter, with the residual volume being primarily hexane/chloroform.

For children's samples (those under 12 years) we found that the total amount of sebaceous material was often minimal; therefore, one-half of the entire sample had to be consumed in order to obtain analyzable material when the samples involved children.

The free fatty acids and neutral organic compounds collected in this manner were then derivatized with diazomethane, converting the fatty acids into the more volatile methyl esters. We have found diazomethane, prepared from N-methyl-N-nitrosourea, to be a superior method for generating methyl esters at ambient temperature [2]. Generally the products formed are nearly free of undesirable side reactions. The procedure for generation of diazomethane is outlined below.

Production of diazomethane involves stirring an ethereal slurry of N-methyl-N-nitrosourea (Pfaltz and Bauer Inc., Waterbury, CT) over an ice cold 40% potassium hydroxide (KOH) solution. The yellow diazomethane/ether solution is simply decanted off for refrigerated storage. In this way, up to 50 mM solutions of diazomethane can be produced, which are relatively stable for weeks. The methylation is done by dropping the yellow diazomethane solution onto the sample until the yellow color persists (or the evolution of nitrogen ceases). For a typical fingerprint sample, only 4-8 drops from a disposable pipette is necessary.

The samples were allowed to react with diazomethane for about 10 minutes, then the samples were reduced to near dryness. This procedure allows volatile methyl ethers (traces of which are present in the ethereal diazomethane solution) to evaporate without loss of the heavier fatty acid methyl esters. This method was tested with samples of octanoic acid methyl ester and found to provide 95% recovery of the methyl ester, indicating that volatile loss is minimal for C8 acids, and will thus be workable for any methyl ester of C8 chain length or larger. The samples

were then transferred to limited volume (100 microliter) gas chromatograph sample vials with a 20 microliter portion of acetone. The known volume of transfer solvent allowed for an accurate quantitation of each identified component.

Gas chromatography / mass spectrometry (GC/MS) was used as the analytical assay for the content of each sample. The instrument used was a Hewlett Packard 5890 GC coupled with a Hewlett Packard 5971 Mass Selective Detector (MSD). The mass spectrometer was used in electron ionization (EI) scan mode, monitoring ions from 40-500 daltons, the sampling rate equal to 1.3 seconds per scan. The chromatographic conditions used are listed in Table 2.

TABLE 2. Gas Chromatograph Instrument Conditions

Injector temperature:	320 °C,
Transfer-line temperature:	300 °C,
GC temperature program:	initial temperature at 50 °C, hold for two minutes, temperature ramp 1 at 15 °C to 150 °C, temperature ramp 2 at 8 °C to 280 °C, hold for 2 minutes, temperature ramp 3 at 10°C to 340°C, hold at 340°C for 6 minutes.
Analytical column:	Restek® RTX-1 crosslinked polydimethylsiloxane column. 0.25 micron x 0.25 mm x 30 m.
Column head pressure:	10 psi helium.

The temperature program provided adequate separation of the lighter fatty acid components, while minimizing the separation time for larger components in the squalene and wax ester region of the chromatogram. A high temperature injector condition and high transfer line temperature was imperative for obtaining an optimal signal to noise ratio for cholesterol (and presumably for other steroids); however, the use of a hot injector was found to require frequent maintenance in order to ensure proper transfer of cholesterol to the column. Cholesterol is often used as a GC/MS performance check (as it is a sensitive and difficult analyte); it is fortuitous that it was also a potential target for this study.

4.0 ANALYTICAL RESULTS

Markedly different compositions were observed among individuals and between the heavily sampled 12-15 year age group and adults. The differences were primarily ones of percent distribution of the major components, and not differences in overall chemical species. In two instances we asked the same volunteers to give samples on different days. The chromatographic appearance of the volatile fatty acids were comparable to that individual's initial sample in both cases. Because of the observed differences between individuals, it may be possible to exclude an individual as the donor of a fingerprint based on the chemical composition of the fatty materials in the fingerprint. Ordinarily, adult fingerprints were found to contain (in order of abundance) squalene, oleic acid, palmitoleic acid, and palmitic acid. However, there were donors in which the squalene component was minimal or absent, with the fatty acids comprising the majority of the analyzable material. Table A.1 in Appendix A lists the primary volatile fat soluble materials which were found by GC analysis in an average adult print. Major components are listed in bold, and these ordinarily make up the bulk of the analyzable fatty materials in a fingerprint.

For very young children, the samples were nearly devoid of fatty acids and squalene; the GC traces are nearly background levels in all samples we collected. It is assumed that the sebaceous glands are not active in pre-school age children; a larger sampling is necessary to verify the generality of this statement. In the case of children (sampling from a 4th grade class– ages 10 to 11 years old) there were three major groupings that were noted for fingerprint composition. Some in this age group had minimal amounts of fatty acids and squalene, similar to that observed in the younger subjects. Other volunteers in this age group deposited materials which had a fatty acid and squalene composition much like that observed in adults, but in less quantity than that observed in samples taken from adults. Lastly, 4 samples collected from female volunteers in this age group, contained a large cholesterol component. The meaning of this last result is unclear. We could not find a commonly available cosmetic which contained cholesterol as a major ingredient. In these particular samples there was no indication of other common cosmetic ingredients (such as the palmityl wax esters or glyceryl esters common in hand lotions). It is possible that the secretion of cholesterol is an unreported consequence of the maturation process, at least in some individuals. In our experience, cholesterol was not a major

component in any of the adult fingerprints analyzed; the biosynthetic precursor to steroids (squalene) was usually a pronounced peak in the chromatograms.

Cosmetic ingredients form a signature in some chromatograms, often observed in those from adult female volunteers. The materials observed include hydrocarbons (tetracosane to triacontane) from petroleum jelly, short chain glycerides, wax esters (usually palmityl palmitate or palmityl stearate), and branched saturated hydrocarbons such as squalane (hydrogenated squalene). The function of these latter materials is probably to "moisturize" the skin through limiting loss of water through evaporation; their constitution is chemically similar to that observed for native skin secretions. These materials show up as major peaks outside of the normal human secretion pattern. Total ion chromatograms of aged fingerprint samples from a representative subject are provided in Appendix C. Figure C.1 is a total ion chromatogram of the initial pattern, showing the abundant squalene at ca. 26.8 minutes, with the fatty acid group eluting in the 10 – 21 minute range. The heavier wax esters and sterol components are found from 29 – 35 minutes. When samples were aged, they were re-sampled and re-extracted at 10, 30, and 60 day intervals (for adult fingerprints).

A striking problem with our data is the net variability in the subsamples. We chose to merely cut the filter paper material in two and randomly mix the 12 pieces. Further, the method for collection of the samples is at the convenience of the volunteers, making a homogeneous print image impractical. Care was taken to maintain the integrity of the fingerprint samples and their contents by minimizing their exposure to laboratory chemical background and excessive physical handling; the goal was to allow fingerprints to age in "natural" conditions, as they would when held as protected evidence. As Figure C.2 demonstrates, the net amount of fingerprint material in the 10 day sampling is twice as abundant than in the initial sample; Figure C.3 from the 30 day sample is only 1/10 as much as found in the initial sample. However, Figure C.4 (60 day sample) depicts about the same level of overall components as observed in the initial sample. Because of this inherent inhomogeneity, comparative quantitation of individual components over time, is not practical.

Note also that in Figure C.3, squalene is absent, but re-appears in the 60 day sample (Figure C.4), but not at the same relative levels as the day 1 sample (Figure C.1). It is possible that the periphery of the print images (light application) are more subject to degradation of this component, or there may be other factors which cause loss or conversion of this component

(such as microbial degradation). In any case, generalizations can be made from examination of multiple examples from our aging studies and are summarized below:

- Squalene and other multiply-bonded compounds (oleic and palmitoleic acids) undergo significant degradation in a 60 day exposure to air, when compared to the saturated analogous compounds.
- The abundant wax esters in human secretions also have double bonded moieties (one series are the palmitoleic esters). These appear to undergo degradation somewhat more slowly than oleic acid or squalene.
- The saturated acids and saturated wax esters maintain a more constant relative relationship over the 60 day aging period.
- Lighter molecular weight saturated acids (especially nonanoic acid) appear in the early part of the chromatogram of the aged samples..
- Traces of diacids (such as nonadioic acid) are found in aged samples.
- The total amount of material found by our derivatization method decreases for aged samples, probably thorough degradation to smaller molecules.

The literature indicates that air oxidation of unsaturated acids such as oleic prefer allylic positions (one carbon away from the double bond), and that subsequent fracture of the molecule would happen in the δ-8 and the δ-11 positions [3]. The observation of nonanoic acid and nonandioic acid in aged fingerprints indicates that the fracturing of the oleic acid molecule may occur at the site of the double bond. This is an important observation, (though it is very preliminary), in that air oxidation removes a molecular functional group which could be used as a target for reagent development.

The fate of squalene remains unknown. Squalene initially undergoes addition reactions which create chromatographic peaks in front of and after the squalene peak which show the same major ions (m/z 69, 81) as squalene. These apparently are transient species which undergo rapid conversion to other materials; as their concentration never increases to rival the amount of squalene initially present. In samples in which squalene is abundant, there is a new component eluting at 22.5 minutes which exhibits ions which may indicate a stable cyclic structure (m/z 209, 314, 349). None of our libraries indicated a good match for this material; not enough was present in any one sample for further characterization. We believe that this component is a form resulting from the cyclization of squalene into a steroid precursor [4], however the only basis for this conclusion is the apparent growth of this component in a complex medium where squalene is declining. Further examination is worthwhile for this component, since if it contains ketone

groupings or stabilized double bonds, it would make an attractive chemical target for a fluorescent tag.

Quantitation of the initial fingerprint extracts was accomplished on 9 randomly chosen 8-12 year old subjects, and 9 adult subjects. Quantitation is estimated as ng per component in a single fingerprint impression. Subsampling of the entire sample and multiple impressions by the donor onto the surface have been factored into this estimation. Table A.2 in Appendix A details the major peaks present in the chromatograms for these individuals in descending retention time. The material names are abbreviated (so that C14 sat is to be read as 14 carbon saturated acid – myristic acid) and the compounds were estimated by quantitation versus similar compound types. We chose as standards stearic acid as a representative for the saturated acid group, oleic acid as a representative of the unsaturated acids. Wax esters were estimated as having similar response to the methyl esters (stearic, oleic) above. Squalene and cholesterol were quantitated versus the authentic materials.

5.0 PHYSICAL DEVELOPER ELECTRON MICROSCOPY

In an effort to ascertain the mechanisms of the one available reagent system which appears to interact with fatty components of fingerprints, a series of high resolution electron micrographs were taken of aged fingerprints which were developed in silver–based physical developer solution. The formulation of the physical developer follows the established procedure used by the United States Secret Service (provided by Robert Ramotowski) and is detailed below.

- Physical Developer (PD) Reagent
  - Deionized water (900 mL)is used to sequentially dissolve the following materials: 30 g ferric nitrate, 80 g ferrous ammonium sulfate, and 20 g citric acid.
  - A liter of water is used to disperse 4 g n-dodecylamine acetate and 4 mL Synperonic –N (nonoxynol-9) to make a detergent solution.
  - Distilled water (100 mL) is used to dissolve 20 g of silver nitrate. A pre-wash solution is made by mixing 25 g maleic acid in one liter of water.

Prior to use, the first solution of ferric/ferrous couple (900 mL) is mixed with 40 mL of the detergent solution and 50 mL of the silver nitrate solution. Since papers are hardened with calcium salts, the paper must be rinsed in the maleic acid pre-wash to render the paper surface neutral to acidic (solubilizing calcium), and may be rinsed once with a bath of deionized water.

- Development

Using a tray with the PD solution in it, the paper bearing the fingerprint is allowed to interact with the redox solution and deposit silver to the desired degree of development (operator dependent). No studies of the effect of additional time in the PD developer were conducted. A few prints from volunteers were selected from the > 60 day aging study and subjected to the PD development process. Of the paper where there was apparent ridge detail (without smudging) 1 cm^2 samples were given to the electron microscopy laboratory for imaging.

- Electron Microscopy

The samples were lightly coated with carbon to prevent charging of the surface. Electron micrographs in high resolution / field emission mode have been examined and stored on the computer system. Energy dispersive x-ray (EDX) microprobe examination of the areas around the silver particles did not reveal much additional information about the elemental composition of the areas around the silver image; there does not appear to be any measurable concentration of iron, calcium, or other metals which is acting as a directing influence on the placement of the silver particles in the image. So far, we can only say that there is a collection of larger particles of silver (ca. 7 micron diameter) in the area of the print image than in areas without the print image. An underlying structure of extremely small silver particles (ca. 100 nm or smaller) appear to be more concentrated in the areas of the print. The morphology of the larger particles indicate that they possess much surface area (and are formed from collected silver crystals from the solution) and the overall spherical nature of the 7 micron silver particles supports the notion that these are formed in suspension in the solution. These larger particles are selectively deposited on the paper surface so that a larger net number of these particles make up the visible image of the developed latent fingerprint. There does not appear to be a direct mechanism which attracts silver to fatty residues on the paper; however, there are particles which show apparently fluid bridges between the silver particles and the surface of the paper in the areas which show ridge detail. More commonly, the larger particles are just more concentrated in the areas of visible ridge detail.

An experiment was independently conducted by Jim Young (EMSL) on the areas of the samples which contain fingerprint ridge detail. Mr. Young looked for the K-alpha backscatter X-ray for silver as a sensitive probe for the overall diffuse concentration of silver in the cellulose

matrix. The test was to ascertain if there exists a larger component of nanometer sized particles of silver in the areas of the fingerprint image. Electron micrograms of a fingerprint sample are shown in Appendix B. Figure B.1 depicts X-ray backscatter images which indicate that there is indeed a large concentration of extremely small silver particles (below the resolution limit of the EM system) concentrated in the area of the fingerprint ridge. The concentration of these small particles is generally less in the areas which do not exhibit ridge detail. Though these images are less spectacular than those which show the large particle morphology of the silver imaged fingerprint (Figure B.2), the interpretation of these electron micrographs is believed to be very important. Drawing from the multimetal deposition process [5], the PD process may in fact be driven by electrostatic forces associated with the deposition of silver particles of nanometer size. These extremely small particles then provide a "template" to attract larger spheres of silver formed in the solution (by electrostatic imbalances) to form the visible silver image of the latent fingerprint. Further work in this area is warranted to develop a theory of the PD process.

6.0 CONCLUSIONS

The data collected show that the principle volatile fatty components (up to molecular weight 500) of a fingerprint image consist of fatty acids, steroid precursors (as squalene), and wax esters. Upon aging, various degradation processes serve to shorten and oxidize those components with unsaturated moieties in the molecule. This circumstance removes a principle chemical functional group, which could be used as a chemical "handle" to attach a fluorescent tag to the fingerprint image.

The fingerprint image apparently becomes hardened and less susceptible to partitioning of coloring agents through a number of processes. The first process which contributes to the hardening of the print is due to loss of moisture. Initial experiments were performed on glass slides which indicated loss of up to 85% of the fingerprint's weight (presumably as water) over a two week timeframe. The consolidation of the materials in the fingerprint to a waxy layer decreases the surface area for contact with reagents which might be used to partition with the fingerprint image (cf. the inability of Nile Red to partition into aged prints).

Secondarily, there are chemical changes that serve to consolidate the saturated fatty acids as the major components of the fingerprint image while air oxidation products of the unsaturated components form. The air oxidation products and saturates tend to have a more orderly crystal structure than the unsaturates, leading to a harder, more crystalline surface in the older prints [3].

Squalene is the principle unsaturate in many fresh fingerprints. This material possesses 6 head-to-head allylically coupled double bonds. The available evidence seems to support the production of hexandioic and pentandioic acids as end products from the air oxidation of squalene, with intermediate oxidation products which may be epoxides or ketones by reaction with oxygen, or alcohols and hydroperoxides associated with direct oxidation of squalene at the allylic positions by atmospheric oxygen. The end fate of squalene probably is toward the most fully oxidized forms (pentandioic and hexandioic acids). In any event, the oxidative process appears to remove the double bond functionalilty from consideration for an attachment point of a molecular fluorescent tag.

The process observed in the consolidation of fingerprint components is analogous to that observed in any number of natural product "drying oils" such as Linseed Oil [6] which contains various unsaturated and saturated fatty acid components as glycerides. These darken and thicken

with exposure to air (undergoing oxidations similar to those thought to occur above) with the resulting material hardening into a varnish.

These competing processes severely limit the potential for creation of a chemically active taggant to add onto the existing molecular structure of the fingerprint components. The chemistry of organic acids is fairly limited. Severe reagent conditions are necessary to convert organic acids into reactive species; direct reaction to the organic acid functionality is therefore limited to harsh reactant conditions. The most mild conversion reagent, N,N'-dicyclohexylcarbodiimide (abbreviated DCC) is often used to activate acids in peptide coupling reactions [7]; however, the reaction conditions used for DCC coupling are such that heat and solvent interactions would undoubtedly destroy the fingerprint image upon the substrate while the conversion is taking place. Fingerprint lipid components therefore, lack a foundation from which a reactive agent can directly chemically couple to the materials in the fingerprint. The amount of unoxidized unsaturated acids and various oxidized species which arise from the unsaturates could be a candidate for chemical reactivity; however, the longevity of these species (in relation to the fully oxidized acids) is doubtful. Squalene appears to build a steady state concentration of oxidation products, based on the mass spectrometric evidence, but these components never become as large as the initial squalene concentration, and disappear in severely aged prints.

There is considerable variation between individual prints obtained from our subject base. Most adults have an identifiable suite of fatty acid related components which identify sebaceous secretions. Very young subjects do not secrete sebaceous material to any large degree and apparently afford mostly aqueous saline for the print image. Adolescents, on the other hand, afforded anomalous samples in our study. Some adolescents afforded prints that were "blank", or saline related; others appear to secrete sebaceous material similar to adults. A few samples were collected in which cholesterol was the major component, far exceeding the concentration of all other components in the print. This phenomenon is very interesting, and should be subject to further investigation. Upon aging, the cholesterol laden prints apparently degrade to other materials; though cholestadiene or cholestenones were not detected as major components in the aged samples from these individuals.

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APPENDIX A

ANALYTICAL GC/MS DATA: LISTS OF PRIMARY COMPOUNDS OBSERVED IN SAMPLE FINGERPRINTS

TABLE A.1. List of primary volatile fat soluble materials found in adult fingerprints.

Component	GC retention time(min)	Remarks
Nonanoic acid	8.60	
Adipic acid	8.62	
Dodecanoic acid	12.0	
Tridecanoic acid	13.2	
Isomeric C-14 sat acid	14.02	branched chain acid
9-Tetradecenoic acid	14.19	9 unsat. probable
Tetradecanoic acid	14.46	
Isomeric C-15 unsat. acid	15.0	
Isomeric C-15 sat. acid	15.06	
Isomeric C-15 sat acid	15.4	12-methyl branch possible
Pentadecanoic acid	15.70	
Isomeric C-16 unsat acid	16.2	7 or 9 unsaturation
Isomeric C-16 sat acid	16.4	
Palmitoleic acid	16.68	7-Hexadecenoic acid, major
Palmitic acid (C-16)	17.00	Major Component
9-Hexadecenoic acid	17.5	probable structure
Isomeric C-17 sat acid	17.6	
Isomeric C-17 unsat acid	17.9	
Margaric acid (C-17)	18.2	
Squalene oxidation prod	18.5	m/z 69,81 predominate
12,15-Octadecadienoic acid	18.85	Isomeric to Linoleic
Linoleic acid	18.97	unsats at 9,12 on C018 chain
Oleic acid	19.08	Major component
Isomeric C-18 sat acid	19.20	
Squalene oxide fragment	19.3	MS pattern match to squalene
Unknown	19.38	m/z 101 119,(aldehyde?)
Stearic acid	19.4	moderate component
Trans-C-18 unsat acid	19.8	inferred from mass spec.
Isomeric C-20 dienoic acid	20.8	probable 8,11 diene
Isomeric C-20 unsat acid	21.1	probable 11 ene
Squalene aldehyde fragment	21.3	library search as Branched dien-al
Unknown	21.7	m/z 239, 299
Eicosanoic acid (C-20)	21.8	
Steroidal component	22.7	Similar to androstane m/z 245,261,304 prominent
Eicosanoic acid (C-21)	23.6	
C-22 Trienyl acid	24.6	m/z 348
Isomeric C-22 sat acid	24.88	m/z 354
C-22 unsat acid	24.95	m/z 352
Docosanoic acid (C-22)	25.1	m/z 354
Isomeric C-23 sat acid	26.18	m/z 368
Tricosanoic acid (C-23)	26.32	m/z 368
Squalene oxidation prod	26.4	
Squalene	26.8	Major Component
Squalene oxidation prod	27.5	m/z 69,81 as in squalene May be hydroperoxide
Isomeric C-24 acid –sat	27.8	
Tetracosanoic acid (C-24)	28.1	
Squalene oxidation prod	28.3	aldehydic

Component	GC retention time(min)	Remarks
Diglyceride (C-12 acids)	29.8	probable diglyceride with C-12 or C-14 fatty acid res.
Wax ester,. C-16 acid	30.18	probable C-16 acid, C-16 alc
Wax ester, C-16 acid	31.1	similar to above
Cholesterol	31.13	Minor component
Wax ester,Sterol-Oleic	31.6	Sterol Oleate probable
Wax ester	32.1	similar to above
Steroidal component	32.3	ions similar to cholesterol
Steroidal component	32.5	ions similar to cholesterol
C-26 sat. acid	33.2	
Wax ester Stearic-Sterol	33.8	probable structure: Stearol Stearate
Squalene oxide prod	34.0	hydroperoxide related?
Squalene oxide prod	34.8	m/z 411
Wax ester	35.0	m/z 236
Wax ester	35.8	m/z 236 (unsaturated chain)
Wax ester	36.5	m/z 236, 278
Wax ester	37.1	m/z 236

TABLE A.2. Quantitative data of major components found in representative fingerprint samples.

Sample Identification	t_r[a]	Compound Name	ng/print
11404: male, 8 to 12	30.49	cholesterol	100
	28.50	C26 Sat	3
	27.42	squalene	114
	26.23	C24 Sat	8
	22.10	C20 Sat	4
	19.86	stearic	29
	19.53	oleic	45
	17.44	palmitic	100
	17.12	palmitoleic	63
	16.18	C15 Sat	28
	14.90	C14 Sat	35
11408: female, 8 to 12	27.43	squalene	181
	19.84	stearic	16
	19.52	oleic	29
	17.45	palmitic	82
	17.12	palmitoleic	72
	16.17	C15 Sat	27
	14.89	C14 Sat	32
	14.61	C14 unsat	7
	14.43	C14 Sat	8
	13.61	C13 Sat	3
	12.36	C12 Sat	4
11406: male, 8 to 12	30.54	cholesterol	6
	27.42	squalene	56
	19.84	stearic	11
	19.51	oleic	15
	18.65	C17 sat	2
	17.44	palmitic	21
	17.10	palmitoleic	5
	16.16	C15 sat	6
	14.89	C14 sat	8
ce011504: female, 8 to 12	30.52	cholesterol	885
	27.35	squalene	24
	19.81	stearic	4
	17.40	palmitic	9
ce011505: female, 8 to 12	30.67	cholesterol	3297
	27.40	squalene	171
	19.81	stearic	13
	19.48	oleic	15
	17.40	palmitic	34

TABLE A.2. Continued.

Sample Identification	t_r[a]	Compound Name	ng/print
ce011509: female, 8 to 12	30.58	cholesterol	2
	30.52	unsat wax ester	1
	28.48	C26 Sat	3
	27.40	squalene	91
	26.19	C24 Sat	6
	22.70	C20 Sat	4
	19.82	stearic	17
	19.50	oleic	25
	18.63	C17 Sat	6
	17.40	palmitic	47
	17.09	palmitoleic	34
	16.14	C15 Sat	16
	14.87	C14 Sat	16
ce011909: male, 8 to 12	27.37	squalene	78
	19.82	stearic	2
	19.50	oleic	5
	17.40	palmitic	13
	17.08	palmitoleic	7
	16.14	C15 Sat	6
	14.87	C14 Sat	6
ce011906: female, 8 to 12	27.37	squalene	42
	19.81	stearic	4
	19.48	oleic	4
	17.40	palmitic	16
	17.10	palmitoleic	8
	16.10	C15 Sat	5
	14.86	C14 Sat	7
111811: #37, male adult	34.61	unsat wax ester	59
	34.45	unsat wax ester	56
	33.12	unsat wax ester	58
	26.83	squalene	1952
	25.62	tetracosanoic	33
	19.34	stearic	99
	19.01	oleic	316
	16.96	hexadecanoic	457
	16.64	hexadecenoic	330
	15.69	C15	110
	14.43	C14	147

TABLE A.2. Continued.

Sample Identification	t_r[a]	Compound Name	ng/print
100798: sc01, male adult	36.50	unsat wax ester	47
	26.90	squalene	999
	20.58	sat wax ester	93
	20.26	unsat wax ester	86
	19.45	steric	181
	19.17	oleic	1675
	18.25	sat C17	120
	17.96	unsat C17	450
	17.13	sat C16	2149
	16.84	palmitoleic	4326
	15.80	sat C15	499
	15.15	branched C15	115
	14.55	sat C14	978
	14.23	unsat C14	428
	13.23	sat branched	61
	12.88	sat C13	50
111810: #36, female adult	33.13	unsat wax ester	9
	29.98	unsat wax ester	7
	28.28	unsat wax ester	7
	26.74	squalene	328
	19.33	stearic	62
	19.00	oleic	48
	18.15	C17 sat	6
	17.83	C17 unsat	8
	16.94	palmitic	109
	16.62	palmitoleic	61
	16.49	C16 unsat	9
	16.17	C16 unsat	8
	15.69	C15 acid	16
	14.42	C14 sat	30
	14.15	C14 unsat	10

TABLE A.2. Continued.

Sample Identification	t_r[a]	Compound Name	ng/print
111812: #38, male adult	32.43	unsat wax ester	132
	31.67	unsat wax ester	247
	30.87	unsat wax ester	151
	30.00	unsat wax ester	225
	29.06	unsat wax ester	104
	27.04	squalene	7302
	21.05	unsat wax ester	81
	19.53	eladic	441
	19.36	stearic	258
	19.05	oleic	799
	18.81	linoleic	172
	18.40	C17 unsat	229
	18.18	C17 sat	316
	17.87	C17 unsat	402
	17.28	C16 unsat	480
	17.03	C16 sat(palmitic)	1375
	16.69	palmitoleic	1093
	15.74	C15 sat	720
	14.45	C14 sat	606
	14.15	C14 unsat	141
	13.98	C14 sat branch	68
	13.17	C13 sat	89
	12.57	C13 sat branch	67
120101: #46, male adult	34.69	unsat wax ester	36
	33.91	unsat wax ester	19
	30.91	unsat wax ester	19
	26.86	squalene	1007
	25.68	C24 sat	18
	21.64	C20 sat	9
	21.30	C20 ene	20
	21.10	C20 diene	19
	19.39	stearic	44
	19.07	oleic	168
	18.96	Z linoleic	20
	18.84	linoleic	33
	17.00	palmitic	234
	16.68	palmitoleic	224
	16.54	C17 sat	16
	15.74	C15 sat	58
	14.47	C14 sat	87

TABLE A.2. Continued.

Sample Identification	t_r[a]	Compound Name	ng/print
120105: #56, male adult	34.69	unsat wax ester	31
	33.32	unsat wax ester	21
	31.89	unsat wax ester	24
	30.90	unsat wax ester	21
	30.25	unsat wax ester	20
	28.33	unsat wax ester	135
	26.85	squalene	835
	26.09	unsat wax ester	45
	25.68	C24 sat	20
	21.64	C20 sat	21
	21.09	C20 diene	27
	19.40	stearic	156
	19.08	oleic	277
	18.41	linoleic	53
	18.22	unsat wax ester	150
	17.01	palmitic	337
	16.68	palmitoleic	199
	15.73	C15 sat	56
	14.47	C14 sat	95
120106: #57, female adult	30.65	unsat wax ester	11
	29.77	unsat wax ester	18
	28.81	unsat wax ester	20
	27.74	unsat wax ester	29
	26.79	squalene	176
	26.59	unsat wax ester	26
	19.39	stearic	22
	19.05	oleic	32
	16.98	palmitic	75
	16.66	palmitoleic	28
	15.74	C15 sat	23
	14.47	C14 sat	36

TABLE A.2. Continued.

Sample Identification	t_r[a]	Compound Name	ng/print
121106: #61, male adult	36.43	unsat wax ester	67
	35.29	unsat wax ester	76
	34.66	unsat wax ester	173
	33.87	unsat wax ester	70
	33.16	unsat wax ester	231
	30.87	unsat wax ester	90
	30.01	unsat wax ester	213
	26.97	squalene	5179
	19.35	stearic	103
	19.02	oleic	92
	16.97	palmitic	244
	16.63	palmitoleic	86
	15.70	C15 sat	54
	14.44	C14 sat	72
101904: #14, male adult	38.10	unsat wax ester	39
	36.00	unsat wax ester	91
	34.27	unsat wax ester	136
	32.74	unsat wax ester	150
	31.14	unsat wax ester	205
	28.18	squalene	1893
	26.90	C24 sat	36
	22.65	C20 sat	22
	22.34	C20 unsat	58
	20.40	stearic	188
	20.11	oleic	660
	19.20	C17 sat	53
	18.90	cyclic C18	174
	18.02	palmitic	723
	17.71	palmitoleic	1048
	16.71	C15 sat	173
	15.42	C14 sat	276
	14.10	C13 sat	21
	12.83	C12 sat	68

TABLE A.2. Continued.

Sample Identification	t_r[a]	Compound Name	ng/print
101903: #13, male adult	38.11	unsat wax ester	71
	36.02	unsat wax ester	152
	34.29	unsat wax ester	216
	32.75	unsat wax ester	233
	31.14	cholesterol	1032
	30.25	unsat wax ester	76
	28.27	squalene	5311
	26.92	C24 sat	69
	22.66	C20 sat	43
	22.34	C20 unsat	84
	20.44	stearic	491
	20.12	oleic	860
	19.21	C17 sat	108
	17.90	palmitic	247
	17.72	palmitoleic	1229
	16.72	C15 sat	377
	15.44	C14 sat	644

a) t_r= Gas chromatograph retention time of component in minutes.

APPENDIX B

ELECTRON MICROGRAMS OF FINGERPRINT SAMPLES

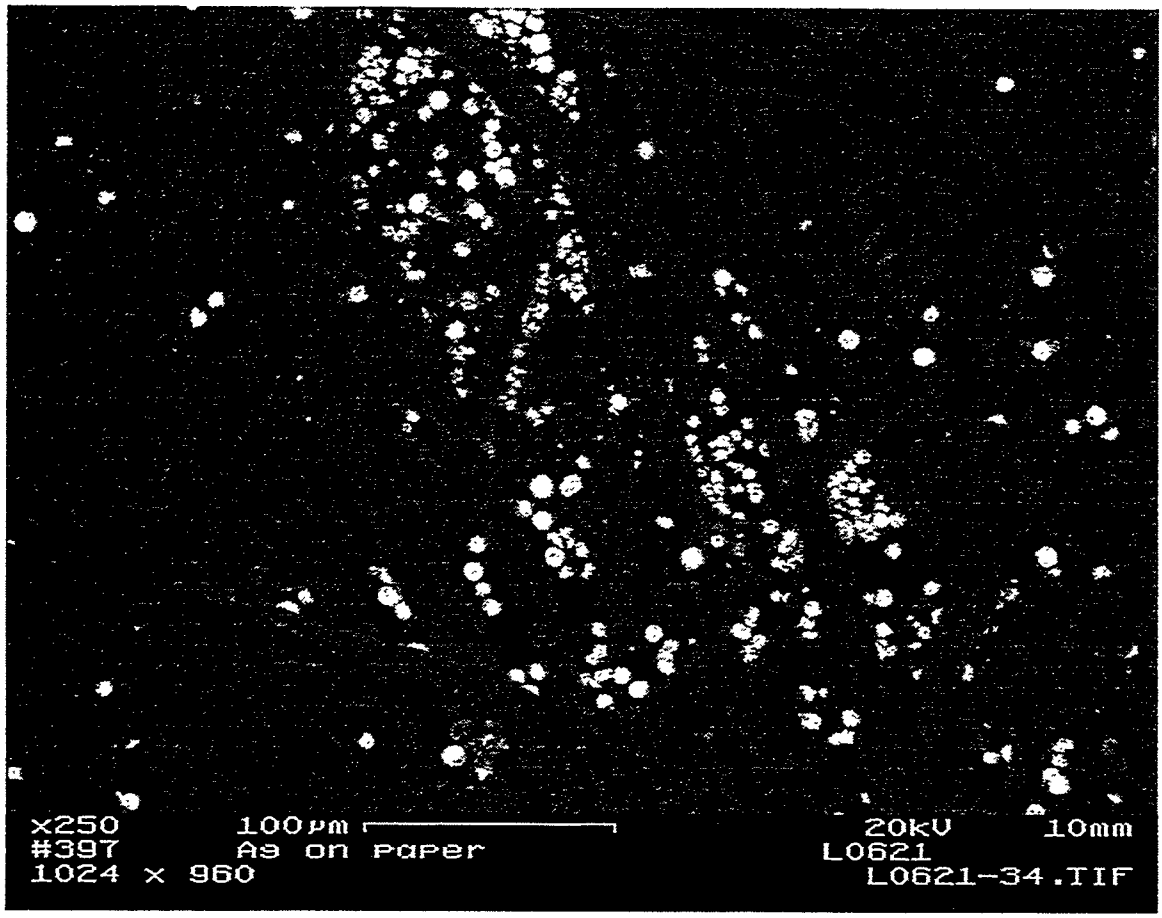

FIGURE B.1. Electron Micrograph of Fingerprint Ridge Detail Indicating Large Concentration of Particles.

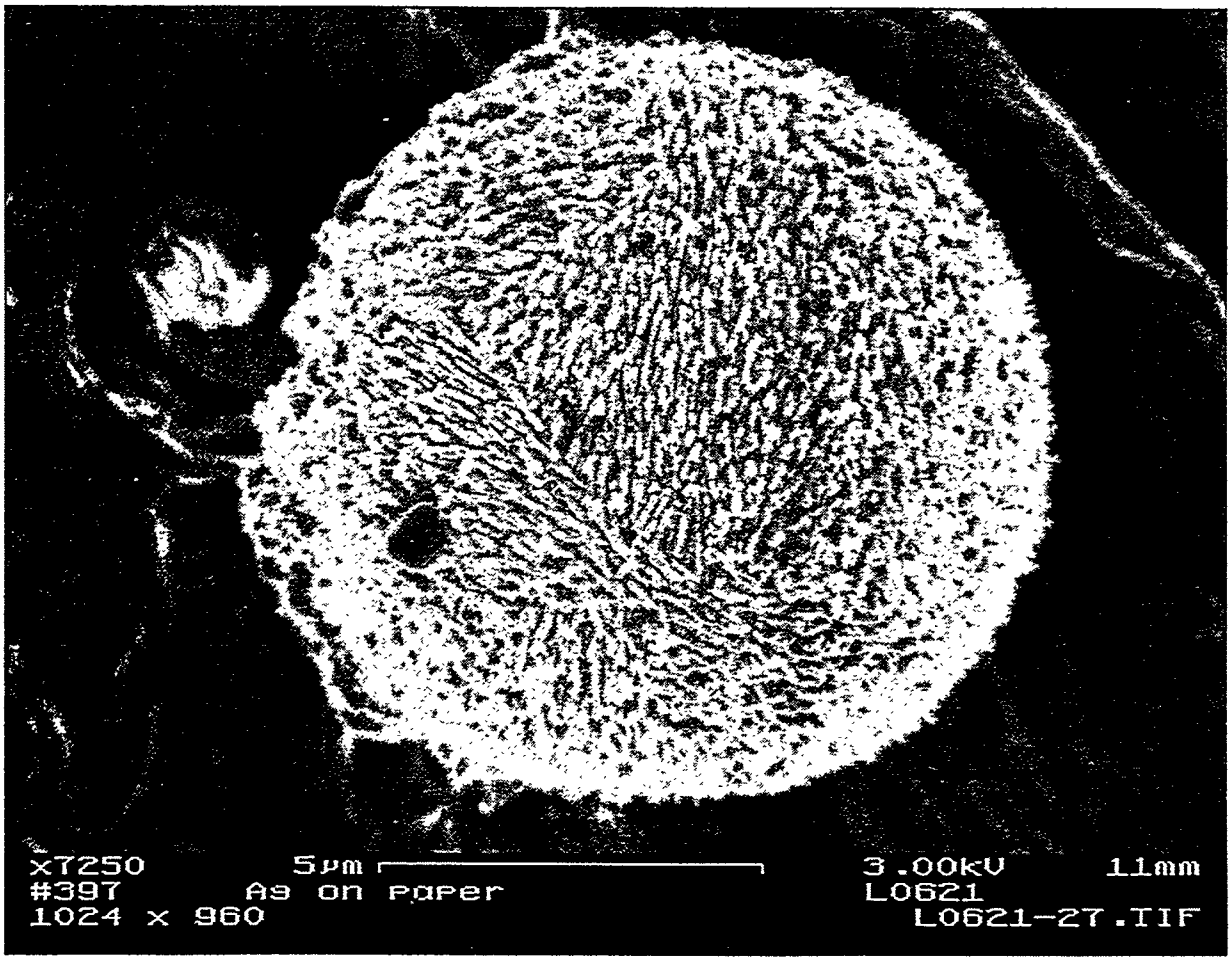

FIGURE B.2. Electron Micrograph of Particle Morphology of the Silver-Imaged Fingerprint, Enlarged Area of Figure 1.

APPENDIX C

TOTAL ION CHROMATOGRAMS FROM GC/MS ANALYSIS OF AGED FINGERPRINT SAMPLES

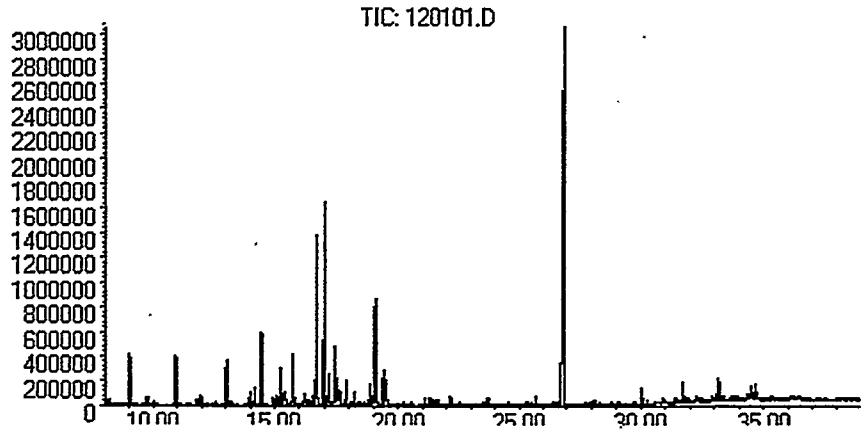

FIGURE C.1. Total ion chromatogram of day 1 fingerprint extract from adult subject depicting squalene as major component at 26.8 minutes.

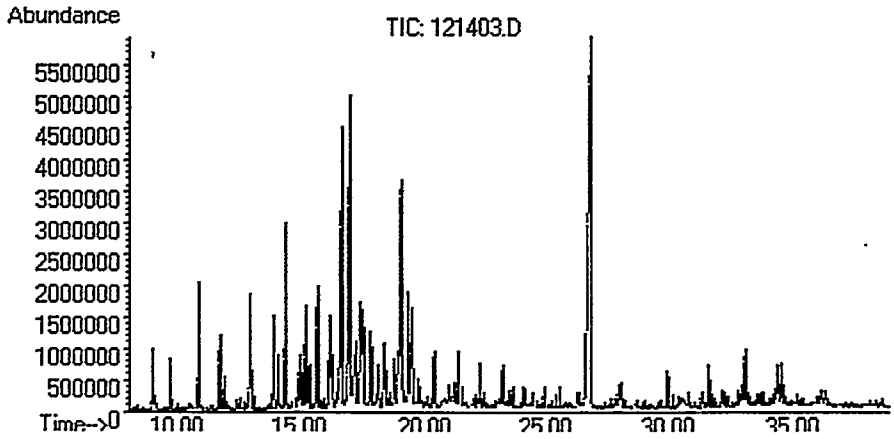

FIGURE C.2. Total ion chromatogram of day 10 fingerprint extract from adult subject depicting squalene peak with increased abundance from day 1 chromatogram.

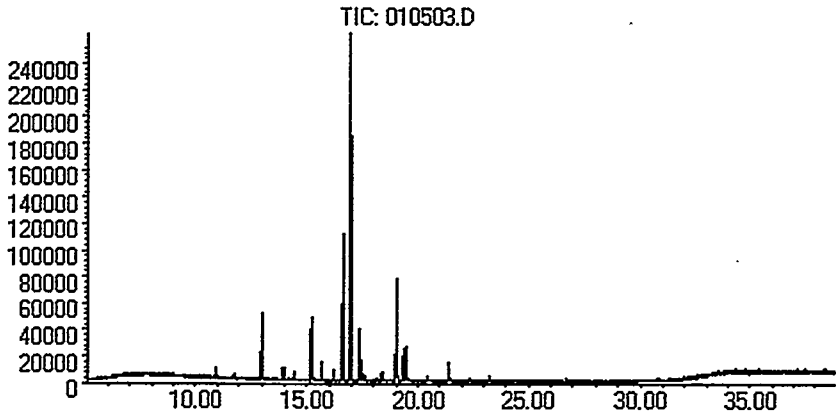

FIGURE C.3. Total ion chromatogram of day 30 fingerprint extract. Fingerprint components are one-tenth of day 1 abundance and squalene is absent.

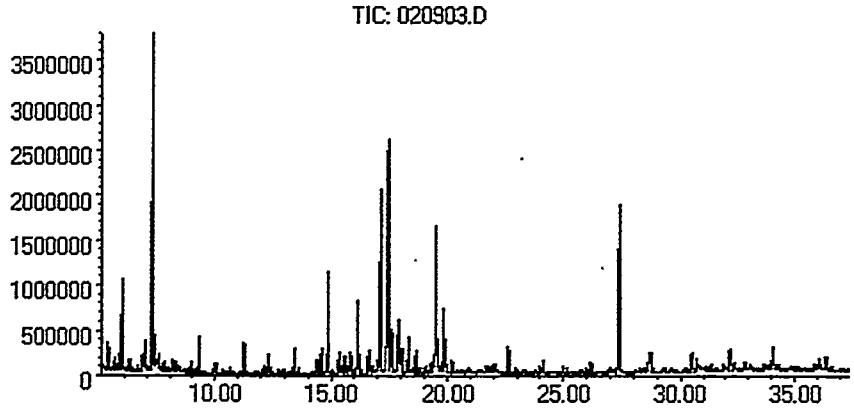

FIGURE C.4. Total ion chromatogram of day 60 fingerprint extract. Fingerprint components are at initial (day 1) abundance, with the reappearance of squalene also at day 1 levels.

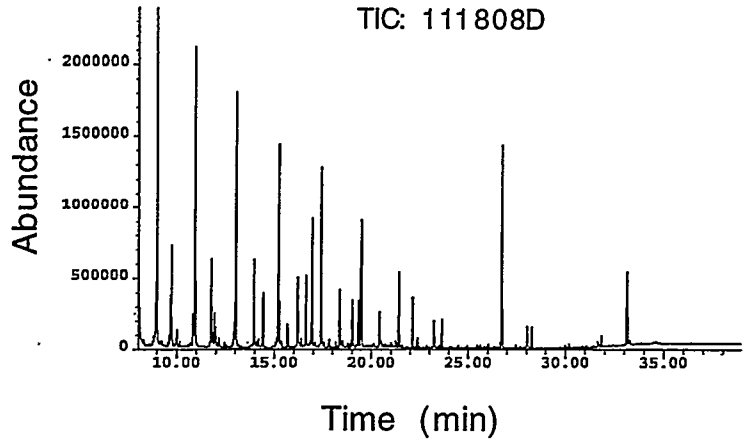

FIGURE C.5. Total ion chromatogram of initial extract from adult female fingerprint (Sample No. 33)

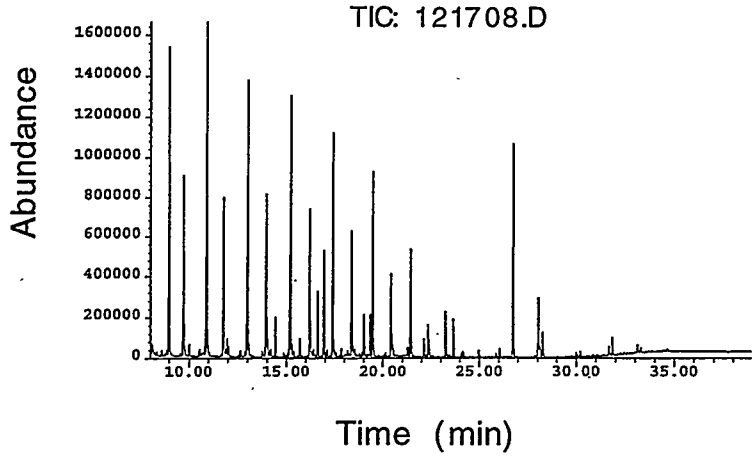

FIGURE C.6. Total ion chromatogram of day 30 extract from adult female fingerprint (Sample No. 33)

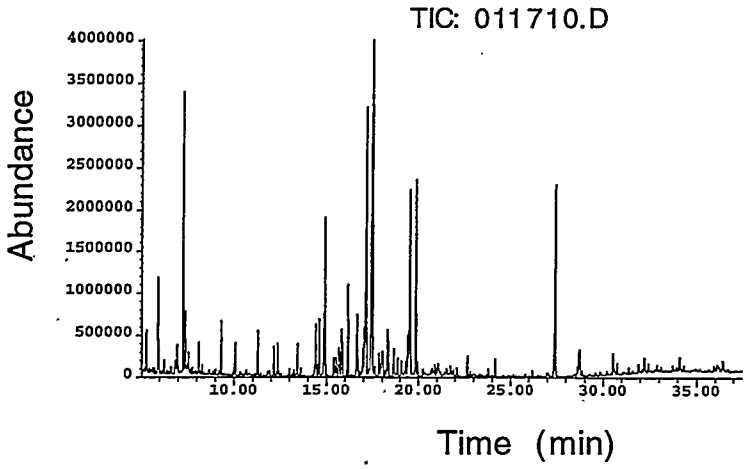

FIGURE C.7. Total ion chromatogram of day 60 extract from adult female fingerprint (Sample No. 33)

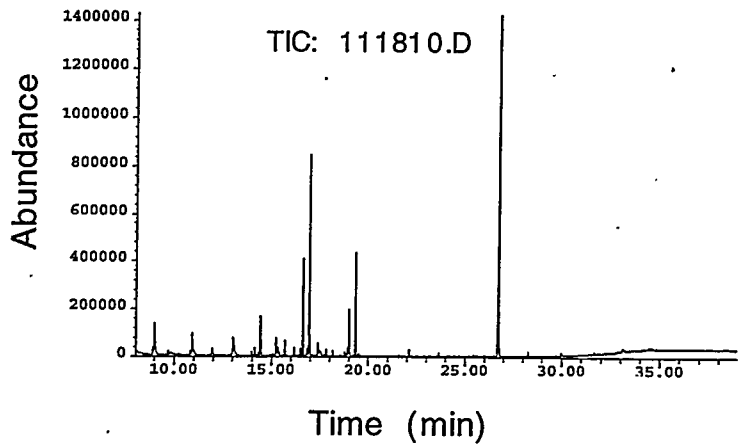

FIGURE C.8. Total ion chromatogram of initial extract from adult female fingerprint (Sample No. 36)

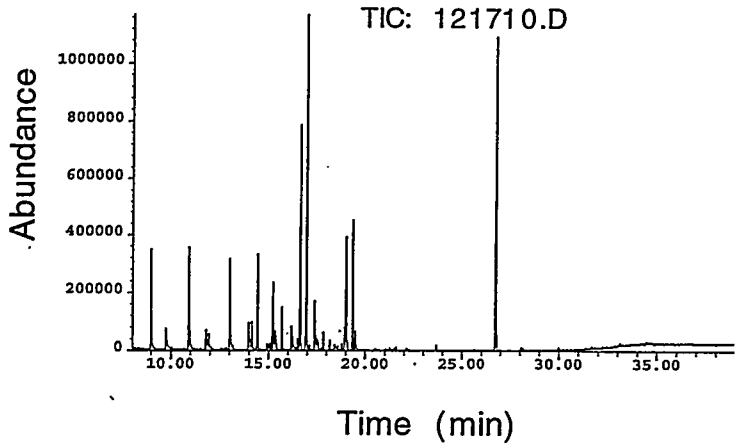

FIGURE C.9. Total ion chromatogram of day 30 extract from adult female fingerprint (Sample No. 36)

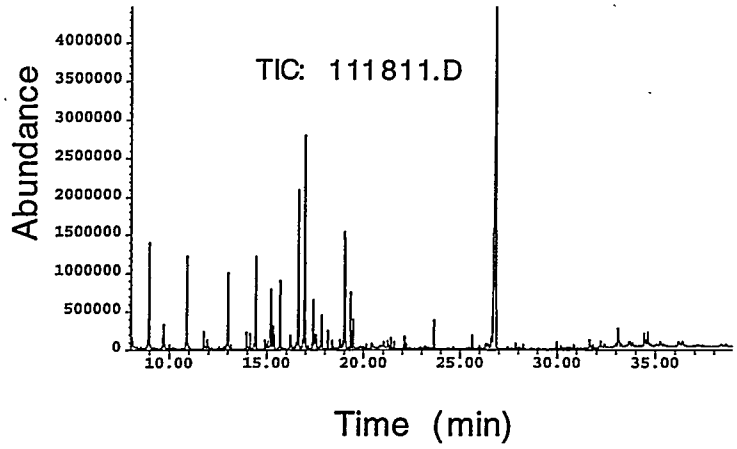

FIGURE C.10. Total ion chromatogram of initial extract from adult male fingerprint (Sample No. 37)

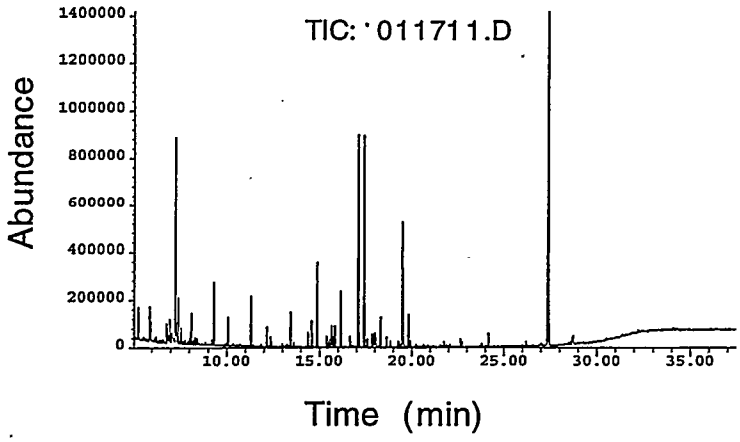

FIGURE C.11. Total ion chromatogram of day 60 extract from adult male fingerprint (Sample No. 37)

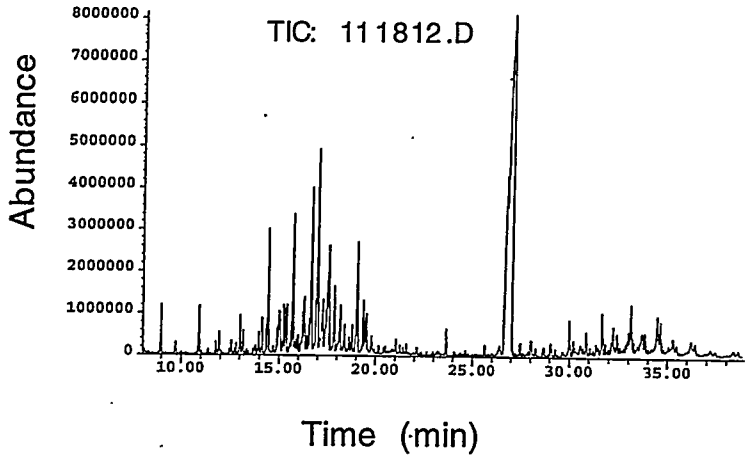

FIGURE C.12. Total ion chromatogram of initial extract from adult male fingerprint (Sample No. 38)

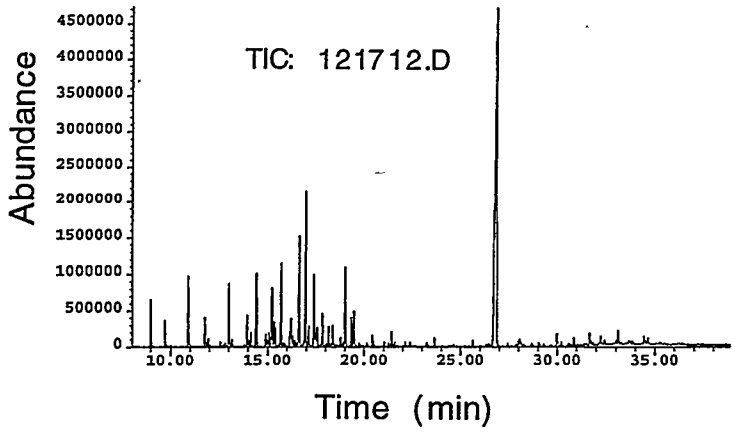

FIGURE C.13. Total ion chromatogram of day 30 extract from adult male fingerprint (Sample No. 38)

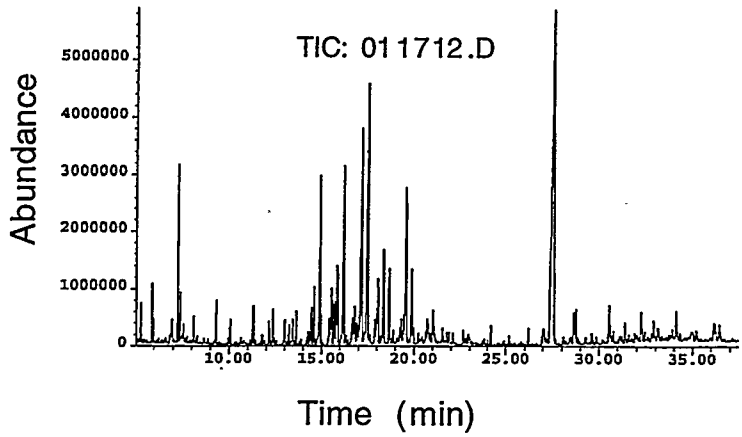

FIGURE C.14. Total ion chromatogram of day 60 extract from adult male fingerprint (Sample No. 38)

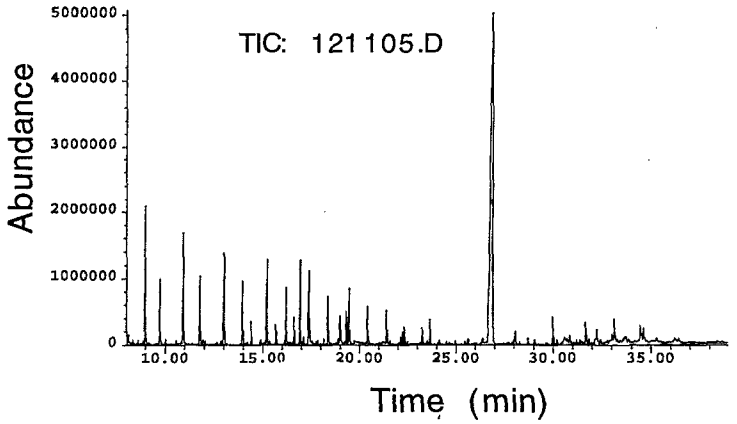

FIGURE C.15. Total ion chromatogram of initial extract of juvenile female (age 8-12) fingerprint (Sample No. 60)

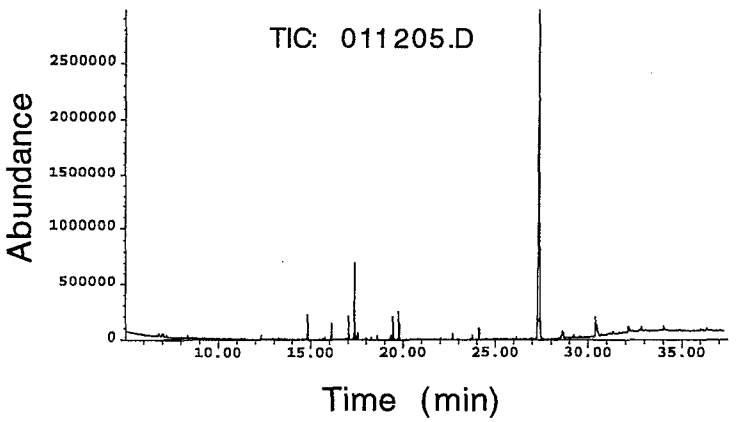

FIGURE C.16. Total ion chromatogram of day 30 extract of juvenile female (age 8-12) fingerprint (Sample No. 60)

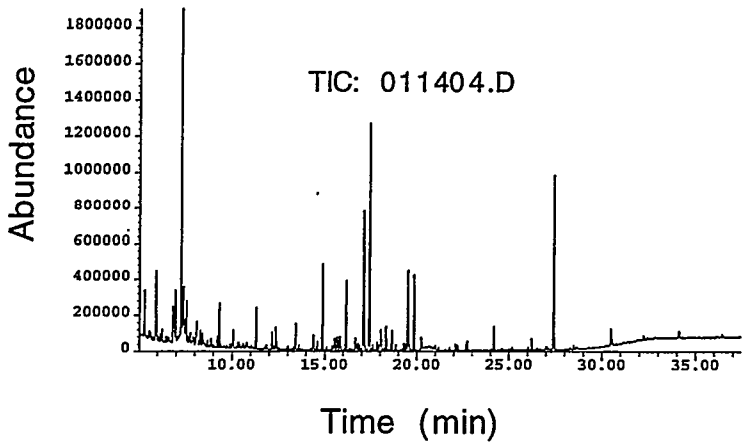

FIGURE C.17. Total ion chromatogram of initial extract of juvenile male (age 8-12) fingerprint (Sample No. 67)

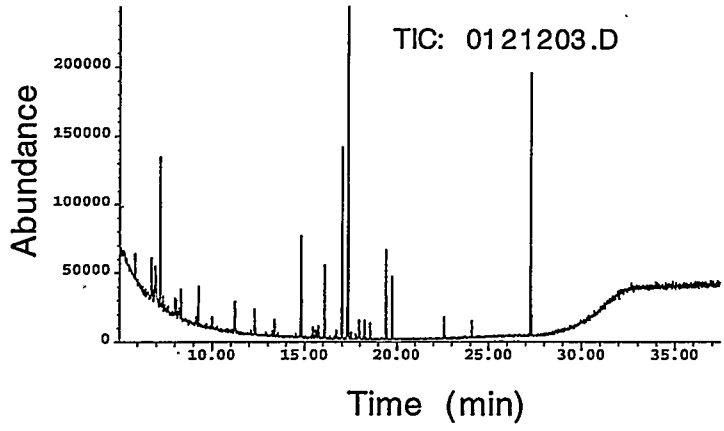

FIGURE C.18. Total ion chromatogram of day 30 extract of juvenile male (age 8-12) fingerprint (Sample No. 67)

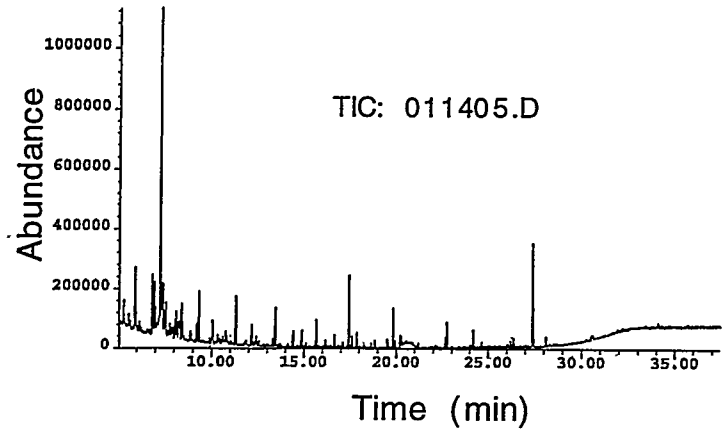

FIGURE C.19. Total ion chromatogram of initial extract of juvenile female (age 8-12) fingerprint (Sample No. 68)

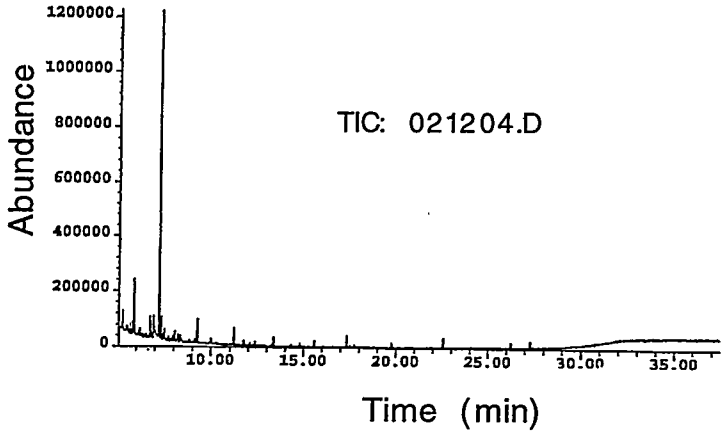

FIGURE C.20. Total ion chromatogram of day 30 extract of juvenile female (age 8-12) fingerprint (Sample No. 68)

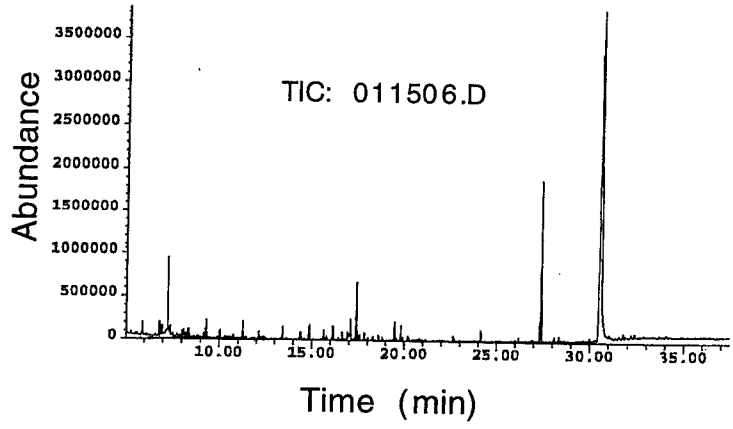

FIGURE C.21. Total ion chromatogram of initial extract of juvenile female (age 8-12) fingerprint (Sample No. 76). Note: major peak is cholesterol.

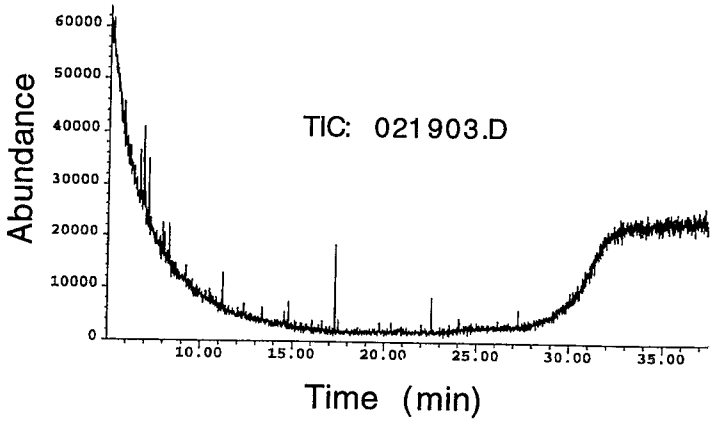

FIGURE C.22. Total ion chromatogram of day 30 extract of juvenile female (age 8-12) fingerprint (Sample No. 76). Note: cholesterol absent.

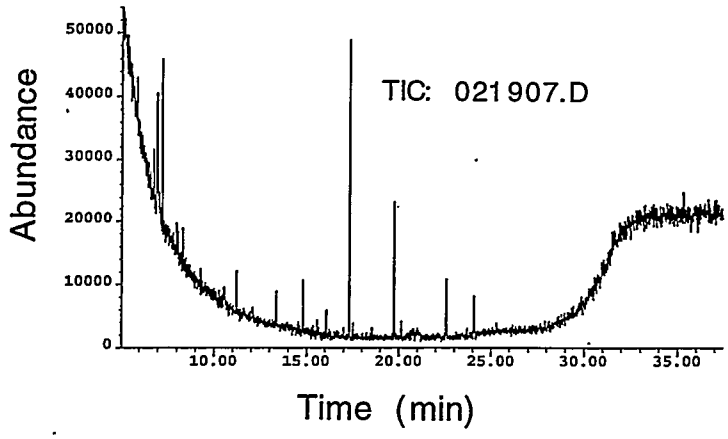

FIGURE C.23. Total ion chromatogram of initial extract of juvenile male (age 8-12) fingerprint (Sample No. 80).

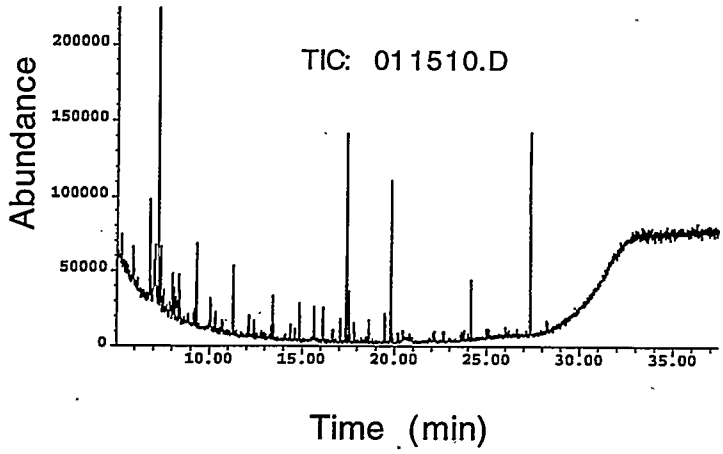

FIGURE C.24. Total ion chromatogram of day 30 extract of juvenile male (age 8-12) fingerprint (Sample No. 80).

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