Synthesis, characterisation and application of novel quinones for the detection of latent fingermarks

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Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of requirements for a degree except as part of the collaborative doctoral degree and/or fully acknowledged within the text.

I also certify that the thesis has been written by me. Any help that I have received in my research work and the preparation of the thesis itself has been acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis.

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Signature of Student:

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Conference presentations

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- 'The use of anthraquinones for the detection of fingermarks on porous surfaces' International Fingerprint Research Group, Switzerland, 2009.
- 'Synthesis of anthraquinones and their use for the detection of fingermarks on porous surfaces.' 5th European Academy of Forensic Science, Glasgow, 2009. (poster)
- 'Preliminary results: Synthesis of anthraquinones and their use for the detection of fingermarks on porous surfaces.' 20th International Symposium on the Forensic Sciences, Sydney, 2010. (poster)
- 'Synthesis of anthraquinones and their application as fingermark detection reagents on porous surfaces.' 6th European Academy of Forensic Science, Hague, 2012. (poster)
- 'Synthesis of anthraquinones and their application as fingermark detection reagents on porous surfaces.' 21th International Symposium on the Forensic Sciences, Hobart, 2012. (poster)

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Abbreviations

AFP	Australian Federal P01/0olice
Ag_2CO_3	Silver carbonate
AQ	1,4-Anthraquinone
AQS	1,2-Anthraquinone-4-sulfonic acid, ammonium salt
AR	Analytical reagent
$CDCl_3$	Deuterated chloroform
CID	Collision induced dissociation
COSY	Correlation spectroscopy
CTAB	Cetrimonium bromide
DFO	1,8-Diazafluoren-9-one
EFP-WG	European Fingerprint Working Group
ESI	Electrospray ionisation
FTIR	Fourier transform infrared
GC-MS	Gas chromatography-mass spectrometry
HAQ	2-Hydroxy-1,4-anthraquinone
HCl	Hydrochloric acid
HOSDB	Home Office Scientific Development Branch
HPLC	High-Performance liquid chromatography
Hr	Hour(s)
HRMS	High resolution mass spectrometry
HSQC	Heteronuclear single quantum coherence
IAI	International Association for Identification
IFRG	International Fingerprint Research Group
JP	Joullié's pink
KBr	Potassium bromide
LC-MS	Liquid chromatography-mass spectrometry
m/z	Mass-to-charge
MAQ	2-Methoxy-1,4-anthraquinone
MMD	Multi-metal deposition

mmol	Millimole
mol	mole
mp	Melting point
MS	Mass spectrometry
Na_2SO_4	Sodium sulfate
NMR	Nuclear magnetic resonance
NQS	1,2-Naphthoquinone-4-sulfonic acid, sodium salt
PD	Physical developer
LC-QTOF-MS	Liquid chromatography-quadrupole time-of-flight-mass-spectrometer/spectrometry
RP	Ruhemann's purple
s	Second(s)
SDS	Sodium dodecyl sulfate
SPR	Small particle reagent
TIC	Total ion chromatogram
TLC	Thin layer chromatography
TMS	Tetramethylsilane
UK	United Kingdom
UTS	University of Technology Sydney
v/v	Volume/volume
VMD	Vacuum metal deposition
VSC	Video spectral comparator
w/v	Weight/volume

Abstract

Identification of an individual through fingermarkss is one of the oldest types of evidence in forensic science. A number of techniques are available for the detection of latent fingermarks on porous surfaces; for example 1,2-indanedione zinc (IND-Zn), 1,8-diazafluoren-9-one (DFO), and ninhydrin. While these techniques produce excellent results, each has their drawbacks. For example, ninhydrin requires secondary post-treatment and cooling with liquid nitrogen to produce fluorescent fingermarks. DFO developed fingermarks are difficult to detect on coloured or highly patterned surfaces. IND-Zn produces a highly fluorescent fingermark, however, under white light little contrast exists between the fingermark and the substrate. Therefore, there is need for research into the development of new fingermark reagents.

Quinones have been used for the development of amino acids in chromatography and biochemistry. Recent research into the use of 2-hydroxy-1,4-naphthoquinone (lawsone) has shown promising results for the development of latent fingermarks on porous surfaces. One of the aims of this thesis was to determine the reaction products between lawsone and three amino acids. These products were elucidated using Fourier transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy and quadrupole time-of-flight liquid chromatography-mass spectrometry (LC-QTOF-MS). The proposed product is hypothesised to be similar between benzoquinones, naphthoquinones and anthraquinones as they differ only by π conjugation.

Another aim of this thesis was to synthesise a variety of quinones with differences in conjugation and substitution in order to compare and determine differences in quantum yield and whether these effects would influence their ability to develop latent fingermarks on porous surfaces. A number of quinones were successfully synthesised and characterised using FTIR and NMR spectroscopy and LC-MS.

In this preliminary study, the synthesised quinones and lawsone were then evaluated as potential reagents for the development of latent fingermarks on porous surfaces. The development conditions, reagent concentration, solvent system, pH, and metal

salts enhancements of each quinone were optimised using amino acids and fingermarks on different porous surfaces. All the quinones that were tested in this thesis did not produce coloured fingermarks and only developed faintly coloured amino acid test strips.

Slight improvements in luminescence were observed when comparing the results of the amino acids and fingermarks developed by naphthoquinones and anthraquinones. This is this is likely due to steric hindrance preventing anthraquinones from forming the desired products. Comparisons were also made between the fingermarks developed by the synthesised compounds and IND-Zn, with IND-Zn developed fingermarks being far superior in luminescence.