

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

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A thesis submitted for the Degree of Doctor of Philosophy (Science)

University of Technology Sydney (UTS)

February 2019

Certificate of authorship and originality

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This research is supported by the Australian Government Research Training Program.

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Acknowledgments

First and foremost, I would like to acknowledge my supervisors, Dr Barbara Stuart and Dr Ronald Shimmon. Barbara, thank you so much for your advice, and feedback.

Ronald, thank you so much for all your help in the lab, your enthusiasm for chemistry is an inspiration. Barbara and Ron, you are truly the best supervisors anyone could ask for and I will be forever indebted to you.

Professor Claude Roux and Professor Chris Lennard your input and encouragement as co-supervisors have been greatly appreciated. Dr Xanthe Spindler, I'm in awe by the number of journal article references you keep catalogued in your head! Dr Linda Xiao, I am grateful your assistance and training with the instruments that were used in this project. Dr Alison Ung, your help in the lab has been so invaluable and thank you for listening to me and providing me with positive comments.

I must acknowledge my parents who have supported me throughout my life and especially during all the years at uni. Thank you for all the sacrifices that you have made so that I could be where I am today. Sheng, your work ethic is incredible and your determination in achieving your goals is inspirational.

All the friends that I have made throughout this PhD have made it more enjoyable than it should be. Amanda, you are the greatest friend anyone could ask for, I am so grateful that uni has brought us together. Now that you are living overseas, we will just have to travel further in search of delicious food! Adrian, the sibling I wish I had; your encouragement and the way you tackled your own PhD was especially motivating as I became a part-time student.

Natasha and Susan, you have both been incredible friends throughout the years. Thank you both for helping me with the LC work, it was really invaluable. Scotty and Mike, you two were a great team especially for Forensics at UTS. Anna, you were way too calm throughout your PhD and you have definitely been a good influence on Dave. Brian, thank you so much for reading my synthesis chapter - it definitely taught me a lot and I am so grateful for your feedback! Emily, I am so glad I met you. You're too funny and the most avid reader!

Thank you again to everyone who has helped me throughout the project from my family, supervisors, friends from before uni to those I made throughout.

Conference presentations

- 'Potential for the use of anthraquinones for the detection of fingermarks on porous surfaces.' NSW Police Fingerprint Conference, Expert Conference, 2009
- '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 fingerprint detection reagents on porous surfaces.' 6th European Academy of Forensic Science, Hague, 2012. (poster)
- 'Synthesis of anthraquinones and their application as fingerprint 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 ₂ CO 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 ₂ SO 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 fingerprints is one of the oldest types of evidence in forensic science. A number of techniques are available for the detection of latent fingerprints 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 fingerprints. DFO developed fingerprints are difficult to detect on coloured or highly patterned surfaces. IND-Zn produces a highly fluorescent fingerprint, however, under white light little contrast exists between the fingerprint and the substrate. Therefore, there is need for research into the development of new fingerprint 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 fingerprints 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 fingerprints 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 fingerprints 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.