

6-(*N,N*)-(Dimethylamino)fulvene: A Potential Precursor for a New Class of Fingerprint Detection Reagents for Paper Surfaces

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The ability to detect latent fingerprints on porous surfaces, such as paper-based documents, is extremely important in resolving criminal cases. Detection methods that target amino acids present in latent fingerprint deposits have achieved widespread use due to the binding of these acids to paper fibres resulting in a good representation of the fingerprint. This communication is the first report of 6-(*N,N*-dimethylamino)fulvene (DMAF) as a novel reagent for the detection of latent fingerprints on porous surfaces. Through observation of undergraduate students showing poor laboratory hygiene, we noted that exposure to DMAF leads to brown staining on the students' skin. We discovered that indeed it can develop latent fingerprints on paper surfaces as pale pink impressions, which are luminescent when illuminated at 505 nm and viewed through orange goggles. The procedure is simple, requiring treatment of the specimen with a solution of DMAF in hexane with subsequent heat treatment. Preliminary experiments indicate that DMAF is reacting with the amino acids present in the latent fingerprint. Unfortunately the proposed technique does not perform as well as currently available approaches, such as 1,2-indanedione/zinc, however DMAF may be useful as "lead" compound for the synthesis of non-ninhydrin based fingerprint reagents.

Keywords: Latent fingerprints; amino acids; paper surfaces; forensic science; photoluminescence

Fingerprints have long been used in police investigations and prosecutions not only as form of identification but also as a highly abundant form of trace evidence.¹⁻⁴ Fingerprints can be used by a forensic investigator to determine whether a person was present at a scene and what objects they interacted with. Unlike other trace evidence such as fibres or hair, fingerprints generally only occur from primary contact and are very difficult to pass along by a third party for secondary transfer.⁴

Latent fingerprints are those formed by transfer of secretions of the skin onto a surface and are invisible without chemical or physical treatment.⁵ Both the chemical composition of a fingerprint and the substrate upon which it has been deposited determines how it can be enhanced for visual examination.^{3, 5-6} The amino acids present in skin secretions are highly relevant to fingerprint enhancement on paper substrates

and a number of amino acid-sensitive reagents are in routine operational use.^{3, 5-10} The most commonly used is ninhydrin, and most operationally used reagents are based on its analogues.^{5, 7-8, 10-11} The visualisation of latent fingerprints on porous surfaces using these reagents can be considered to be the trace detection of amino acids where their spatial distribution needs to be retained for subsequent fingerprint analysis. As recently reported by Chadwick et al. current methods do not detect all available latent fingerprints.¹² Fingerprint detection chemistry therefore shares with other areas of analytical chemistry the constant search for improved selectivity and sensitivity.

In recent times there have been studies into alternative sources for amino acid-sensitive reagents other than ninhydrin and its analogues, in particular those compounds that are known to stain skin. Genipin is extracted from *Gardenia jamaicensis* and *Genipa americana*, and when it comes in contact with skin produces a violet stain.¹³⁻¹⁴ Another example, henna, is a skin and hair dye obtained from the leaves of *Lawsonia inermis* and has been in use for millennia.^{5, 7-8, 10} The compound that causes this staining, lawsone, has been investigated as a fingerprint reagent.⁸ Both lawsone and genipin react with amino acids in fingerprint secretions to produce coloured ridge detail, which is also photoluminescent.^{5, 7-8, 10, 13}

In a similar fashion to lawsone and genipin, 6-(*N,N*-dimethylamino)fulvene (DMAF) is a compound which was discovered to stain skin. An investigation into its potential use as a fingerprint reagent was prompted after an undergraduate laboratory experiment at Curtin University, where it was used as a precursor to azulene.¹⁵ Students with poor laboratory hygiene had found that some of their skin had turned a brown colour after being exposed to the compound. Initial experiments were carried out using left over DMAF from the undergraduate lab.

A solution of this leftover DMAF in hexane was applied to a filter paper upon which a latent fingerprint had been deposited. Once the hexane had evaporated the specimen was heated in an oven for a short period of time. The treated fingerprints appeared as faint pink ridges which exhibited luminescence when illuminated by a forensic light source at 505 nm and viewed through orange goggles (Rofin Polilight PL500; Figure 1).

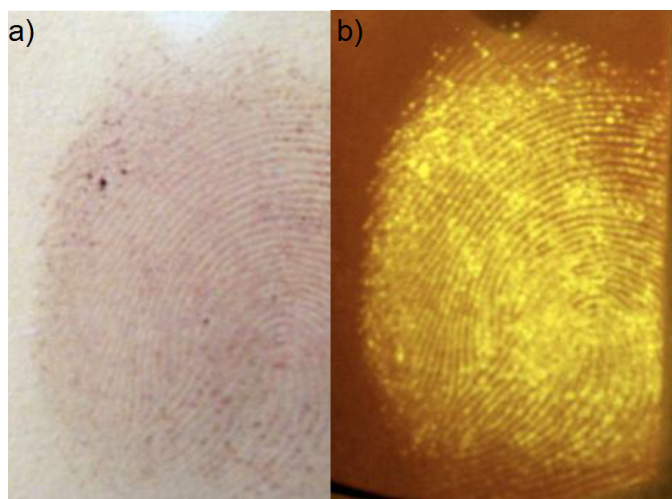


Figure 1: 6-(N,N)-(dimethylamino)fulvene treated latent fingerprint. Images were taken with a Nikon D100 SLR (85 mm focal length, ISO 200): a) absorbance mode (shutter speed 1/30 s and aperture f9); b) photoluminescence mode with excitation using a Polilight PL 500 at 505 nm and viewed through a KV 550 filter, (shutter speed 1 s, aperture f9).

Following this initial successful result, latent fingerprints were collected from a total of 6 donors. The donors' middle 3 fingers on each hand were pressed onto a piece of paper with squares marked on it, this was done 5 times sequentially to produce a 'depletion series' containing 5 sets of fingerprints. The depletion series allows a comparison of fingerprints with varying amounts of skin secretions. Fingerprint treatment conditions are as follows unless otherwise stated. DMAF (80 mg) was dissolved in hexane (100 mL, Mallinckrodt Chemicals). Method development involved the variation of the concentration of the DMAF amount or different solvent combinations. Fingerprint samples were dipped into the DMAF solution contained in a clean glass tray, ensuring that the paper had soaked through and all areas with fingerprints had been covered. These were then left to air dry in a fume cupboard, followed by heat treatment to facilitate the reaction. After heat treatment, pink ridge detail was evident under visible light. When excited by Rofin Polilight PL500 at 505 nm and viewed through an OG550 550 nm camera filter, the fingerprints showed significant luminescence with good contrast.

A preliminary investigation between a laboratory oven and a standard heating press was investigated. The heating press gave much higher background development under visible light and under forensic Polilight. Samples which had been in the oven for 120 minutes had a reduced clarity when compared to the samples which had been in the oven for 30 and 60 minutes. Fingerprints which had been developed for 60 minutes or longer show a much higher level of background development causing parts of the prints to be barely visible.

DMAF dissolves in non-polar solvents, which is advantageous as polar solvents can cause the ink on documents to run preventing further document analysis.^{8,16} Solvents tested include hexane, petroleum spirits 40-60 °C (APS Chemicals), propylene glycol (Merck) and toluene (Sigma-Aldrich). DMAF readily dissolved in toluene, hexane and petroleum spirits; however, preparation in propylene glycol required additional light heating.

The toluene-based reagent caused the ink labels to run, ruining any documents. The petroleum spirits caused high background luminescence, obscuring any fingerprints. Propylene glycol showed some indications of fingerprints but very poor quality. Hexane produced the best quality fingerprints. Unlike other amino acid sensitive fingerprint reagents, DMAF does not require a mixture of different solvents for development, making development solution preparation significantly easier.^{8,16}

Hexane was also compared to 3M™ Novec™ Engineered Fluid HFE-7100, a solvent used to prepare other fingerprint reagents and is the solvent of choice in Australian Police forensic laboratories due to its minimal dissolution of inks.¹⁷⁻¹⁸ The results were comparable as shown in Figure 2, but hexane remained the chosen solvent because of its much lower cost.

Investigations were also performed to determine optimum DMAF concentration. Figure 3 shows a significant increase in the background development, producing fingerprints which are difficult to visualise without image adjustment software. The lowest concentration of 20 mg/100 mL appeared to give the best contrast. However, further investigations indicated that a concentration in the range of 60-100 mg gave more consistent performance. Higher resolution images of fingerprints on paper developed with DMAF are presented in Figure 4. Unfortunately when compared with 1,2-indanedione/zinc, the proposed technique was consistently out-performed.

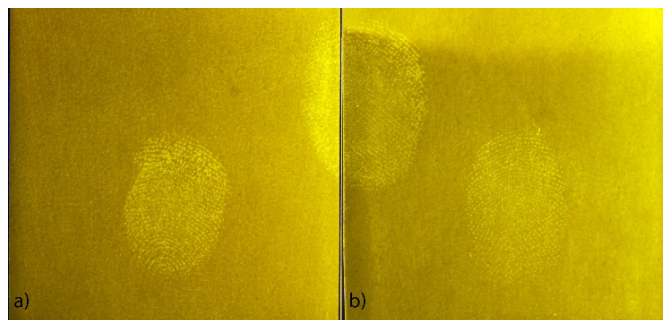


Figure 2: Comparison of HFE-7100 and Hexane when used as a carrier solvent. The fingerprints are from the same donor on the same hand, cut in half down the middle (a) HFE-7100 (b) hexane

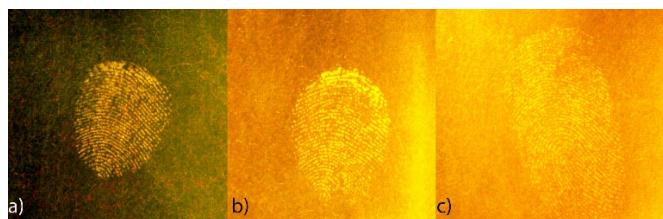


Figure 3: Fingerprints developed with varying concentrations of DMAF in 100mL of hexane. The background luminescence greatly increases with the concentration (a) 20 mg/100 mL (b) 80 mg/100 mL (c) 160 mg/100 mL

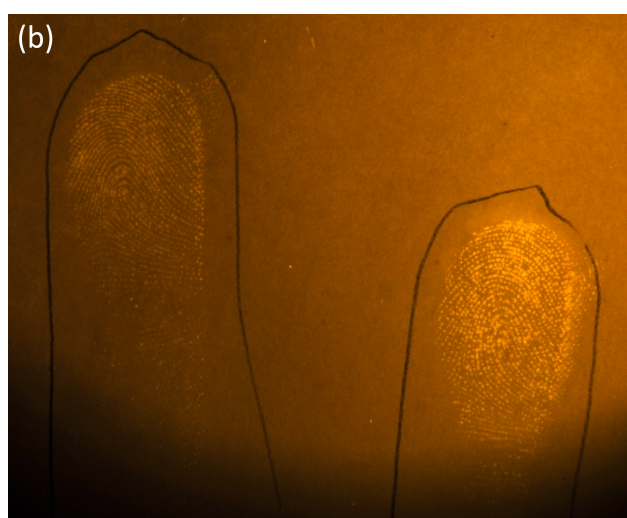


Figure 4: 6-(N,N)-(dimethylamino)fulvene treated latent fingerprints. Images were taken with a Nikon D300 SLR (60 mm focal length, ISO 200): a) absorbance mode (shutter speed 1/40 s and aperture f8); b) photoluminescence mode with excitation using a Polilight PL 500 at 505 nm and viewed through a KV 550 filter, (shutter speed 1/15 s, aperture f8)

A preliminary investigation to confirm that DMAF reacts with amino acids was undertaken. 5, 10, 15, 20, 25 ng per 10 μ L of two major amino acids found in sweat,^{6, 8} alanine and serine were spotted onto paper in 30 μ L aliquots and left to air dry. A "stacked" fingerprints from a single donor was also included for comparison, where the donor stacked all fingerprints from one hand on top of each other to produce a large amount of skin secretions in the one location. Once the spots were dry they were developed in DMAF solution. There was a visible increase in luminescence intensity compared with the water blank. Luminescence intensities of the treated amino acids spots and latent fingerprints were measured using a Cary Eclipse Fluorescence Spectrophotometer with fibre optic attachment (Varian, Mulgrave, Australia), at 580 nm with an excitation wavelength of 505 nm (Figure 5).

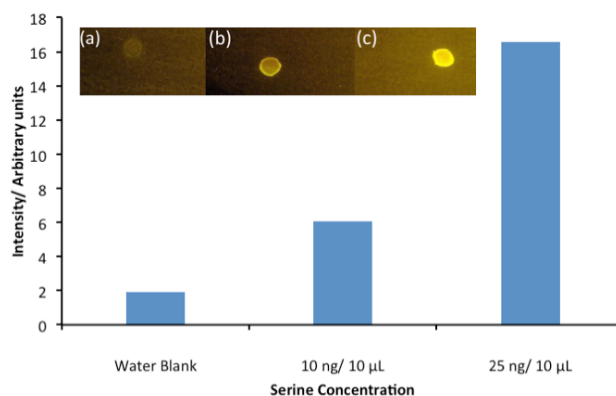


Figure 5: Luminescence intensity of amino acid spots on paper developed with DMAF (λ_{ex} = 505 nm, λ_{em} = 580 nm) (a) water blank (b) 10 ng/10 μ L serine (c) 25 ng/10 μ L serine

Luminescence spectra of the treated amino acids spots and fingerprint were collected over wavelength range 520-650 nm at an excitation wavelength of 505 nm (Figure 6). The spectra obtained from the alanine and serine treated spots has a maximum intensity at a wavelength of 580 nm while the stacked fingerprint's maximum intensity is shifted slightly to the left at approximately 570 nm. This shift in maximum intensity is also evident in similar amino acid tests with genipin.¹³ As secretions from the skin contain a mix of approximately 15 amino acids⁵⁻⁶ rather than just alanine and serine, it is possible that the reaction of the DMAF with individual amino acid species forms a series of unique products.

Scheme 1 shows a proposed reaction pathway for the reaction of DMAF¹⁹⁻²¹ with amino acids. The amino acid replaces the dimethylamine of DMAF followed by a condensation to give the cyclopenta[*b*]pyridine derivative. The amino acid side-chain is retained in the final product which could give rise to the maximum intensity shifts seen in Figure 6.

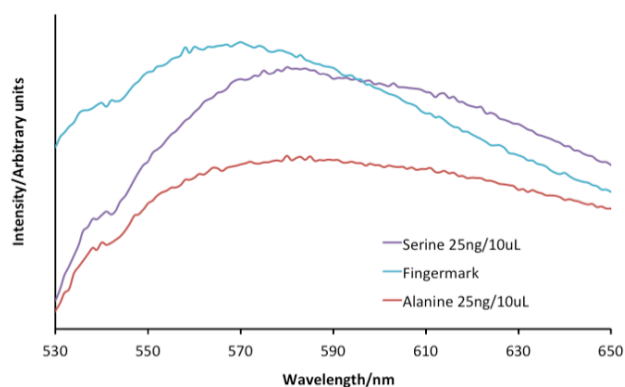
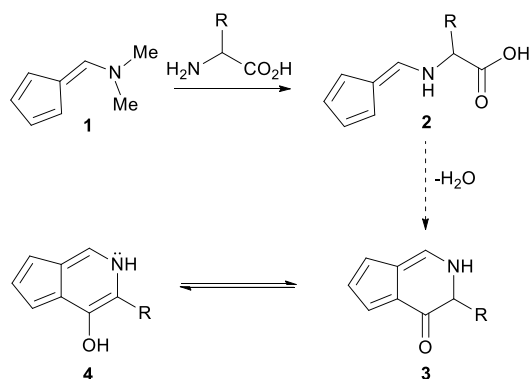


Figure 6: Fluorescence spectra of amino acid spots and a latent fingerprint on paper developed with DMAF (λ_{ex} = 505 nm)



Scheme 1: Proposed reaction mechanism of DMAF with amino acids

This pathway is not confirmed and further investigation and isolation of products is required.

In conclusion while DMAF successfully detected latent fingerprints on paper surfaces, there has to be doubt as to whether it is operationally useful as did not exhibit any significant advantages over the existing reagent 1,2-indanedione/zinc.²² It may however represent a good "lead" compound for the synthesis of non-ninhydrin based fingerprint reagents.

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