Talanta 82 (2010) 1717–1724

Contents lists available at ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Substituted naphthoquinones as novel amino acid sensitive reagents for the detection of latent fingermarks on paper surfaces

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ARTICLE INFO

Article history:
Received 7 July 2010
Received in revised form 26 July 2010
Accepted 26 July 2010
Available online 3 August 2010

Keywords:
Naphthoquinones
Latent fingermarks
Fingerprints
Amino acids
Paper surfaces
Forensic science

ABSTRACT

In this paper, we present our preliminary studies into naphthoquinones as novel reagents for the detection of latent fingermarks on paper. Latent fingermarks deposited on paper substrates were treated with solutions of selected naphthoquinones in ethyl acetate/HFE-7100, with subsequent heating. The selected compounds were 1,4-dihydroxy-2-naphthoic acid, 1,2-naphthoquinone-4-sulfonate, 2-methoxy-1,4-naphthoquinone and 2-methyl-1,4-naphthoquinone. All of the tested compounds yielded purple-brown visible fingermarks, which also exhibited photoluminescence when illuminated with a high intensity filtered light source at 555 nm and viewed through red goggles. Indirect heat using an oven at 150 °C for 1 h was found to be superior to direct heat with an iron, which while providing faster development lead to increased levels of background colouration. Luminescence spectrophotometry revealed differences in photoluminescence characteristics for fingermarks developed with the different naphthoquinones, with excitation over the range 530–590 nm. Luminescence spectrophotometry of developed lysine, glycine and serine spots on paper was used to confirm that the naphthoquinones were reacting with amino acids in the latent fingermark.

1. Introduction

The ability to establish links between persons, objects and locales is extremely important in the course of criminal investigations. The impressions left by the palmar surfaces of the hands, commonly known as fingermarks, are important in this context as they not only demonstrate contact but are also considered sufficiently unique to allow identification of a person [1–3]. The most commonly encountered are latent fingermarks, which are formed by the transfer of natural skin secretions and contaminants from the skin to the substrate. Successful recovery and subsequent analysis of latent fingermarks on a particular substrate relies upon their detection, and a range of physical and chemical methods are available to enable this [1–3]. Fingermark detection chemistry shares with other areas of analytical chemistry the constant search for improved selectivity and sensitivity [4–13].

The substrate is highly influential in determining the most suitable methods for visualisation of latent fingermarks. Paper items such as documents, wrappings and containers are common forms of physical evidence, and establishing who has handled them can be extremely important [1–3]. For paper items, the visualisation of latent fingermarks has predominantly been based on the use of amino acid sensitive reagents [14]. Amino acids are present in the aqueous (eccrine) component of a fingermark deposit and, when transferred onto a paper surface, will adhere with minimal migration as long as the surface is not wet or exposed to high humidity. These amino acid impressions can be very long-lived, and can remain on the substrate for an extended period of time [3].

Ninhydrin (2,2-dihydroxy-1,3-indanedione) was the first amino acid sensitive reagent for developing fingermarks on porous surfaces and is still the most widely used. Ninhydrin reacts with amino acids to form a dark purple coloured compound known as Ruhemann's purple (Scheme 1) [2].

Developed impressions may be further enhanced by treatment with zinc or cadmium salts to produce complexes that exhibit photoluminescence when cooled with liquid nitrogen and excited with a high intensity filtered light source (often referred to as a 'forensic light source') [15].

Since the early 1980s, a range of ninhydrin analogues have been synthesized and tested for their suitability as reagents for the detection of latent fingermarks. Only two of the studied compounds have found widespread operational use; 1,8-diazafluoren-9-one and, more recently, 1,2-indanedione [1,15]

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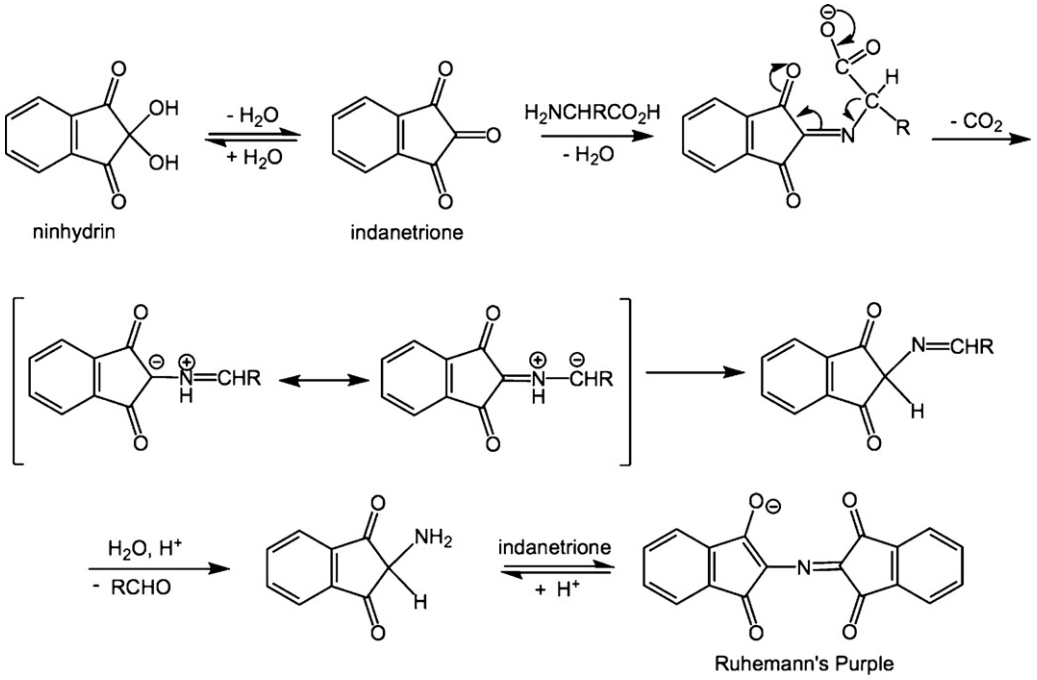
doi:10.1016/j.talanta.2010.07.064



Scheme 1. Reaction mechanism of ninhydrin with amino acids to form Ruhemann's purple [2].

(Fig. 1). These reagents produce developed fingermarks that are photoluminescent at room temperature without further treatment.

The visualisation of latent fingermarks 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 [14]. Prior to 2004, the main focus of research in this area was the further development of compounds related to ninhydrin. An alternative research path has been suggested by Almog and co-workers, with the use of genipin (Fig. 1) as a latent fingermark detection reagent [16,17].

Genipin, which is a natural product, is obtained from a number of plants including *Gardenia jasminoides* and *Genipa americana* L. Extracts from these plants have been used as traditional medicines, food and fabric colourants, and as skin dyes [16,17]. When evaluated for use as a visualization reagent for amino acids on TLC plates, the genipin products were found to have higher molar absorptivities than Ruhemann's purple and were also more stable [16,17]. These observations lead Almog and co-workers to investigate genipin as a fingermark reagent, and it was found that it could develop prints that were both coloured and luminescent [16,17]. Genipin reacts with latent fingermarks on paper to produce blue impressions, with photoluminescence emission occurring at longer wavelengths than for existing treatments. This provides a potential operational advantage by improving the signal-to-noise ratio by shifting the luminescence emission away from any background interference from the paper substrate itself [16,17]. In addition, considering its long past history of human usage, and low cytotoxicity, occupational hazards associated with using genipin are significantly reduced compared to other fingermark development reagents [16,17].

Henna, a natural product sourced from the leaves of *Lawsonia inermis* [18], has been used as a skin and hair dye for millennia, with reports of its use dating back to 1400 BC [18]. The compound thought to be responsible for the staining properties of henna is lawsone (2-hydroxy-1,4-naphthoquinone) (Fig. 2). Prompted by Almog's studies into genipin, we recently investigated lawsone as a potential fingermark reagent for porous surfaces [4]. Latent fingermarks on filter paper surfaces were dipped in lawsone solutions and then heated for 1 h at 140–170 °C. The fingermarks developed as purple/brown prints that were luminescent without further treatment [4]. Further luminescence studies confirmed that the amino acids present in the fingermark deposit were responsible for the developed marks.

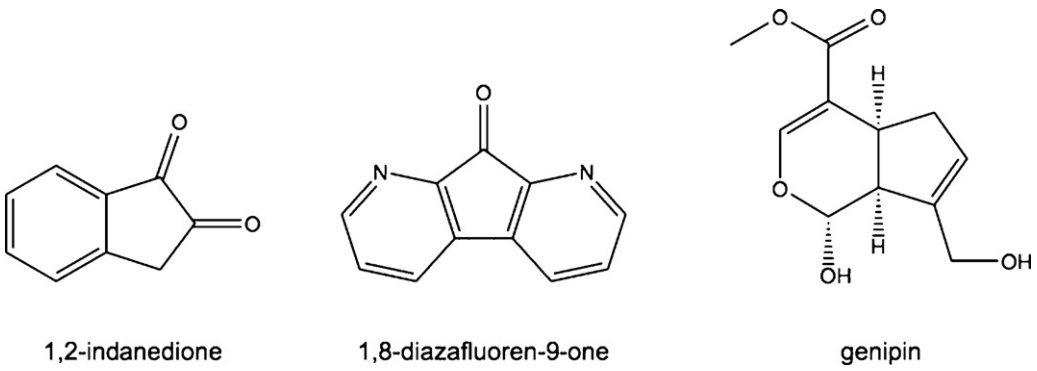


Fig. 1. Structures of 1,2-indanedione, 1,8-diazafluoren-9-one and genipin.