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5-Methylthio Ninhydrin and Related Compounds: A Novel Class of Fluorogenic Fingerprint Reagents

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ABSTRACT: Ninhydrin derivatives bearing sulfur-containing groups at position 5 exhibit excellent properties as fluorogenic fingerprint reagents on paper. Their sensitivity markedly exceeds that of ninhydrin and even that of 5-methoxy ninhydrin. Preliminary experiments indicate it as equal to or better than 1-8-diazafluorene-9-one (DFO). One member of this group, 5-methylthio ninhydrin, has been recently declared an operational fingerprint developer in our laboratory.

KEYWORDS: criminalistics, fingerprints, ninhydrin

Recent years have seen great progress in the fluorogenic development of latent fingerprints on paper and other porous surfaces. The enhanced detectability of latent prints by application of fluorogenic rather than color-development techniques has brought a number of research groups to investigate new potential reagents for fluorogenic visualization of latent fingerprints. Some of these reagents, which react mostly with amino acids, have become quite useful in the case work of forensic science laboratories. Among them are ninhydrin [1,2], 5-methoxyninhydrin [3,4], 4-chloro-7-nitrobenzofurazan (NBD)-chloride [5,6], and particularly 1-8-diazafluorene-9-one (DFO) [7-9]. We wish to report here a new class of such compounds, 5-thioninhydrins (I), which show superiority over existing reagents and in certain aspects even over DFO.

Materials and Methods

Ninhydrin derivatives bearing alkylthio substituents at position 5 (I) were prepared from their corresponding 6-thioindanones (II) by oxidation with N-bromosuccinimide (NBS) and dimethylsulfoxide (DMSO) [10]. The thioindanones (II) were obtained by reacting the corresponding thiolates with the diazonium salt (III) derived from 6-aminoindanone (IV) [11] (Fig. 1). Overall yields were moderate to low, and no attempt was made at this stage to optimize them. 5-Methylthio ninhydrin (Ia) was prepared also by

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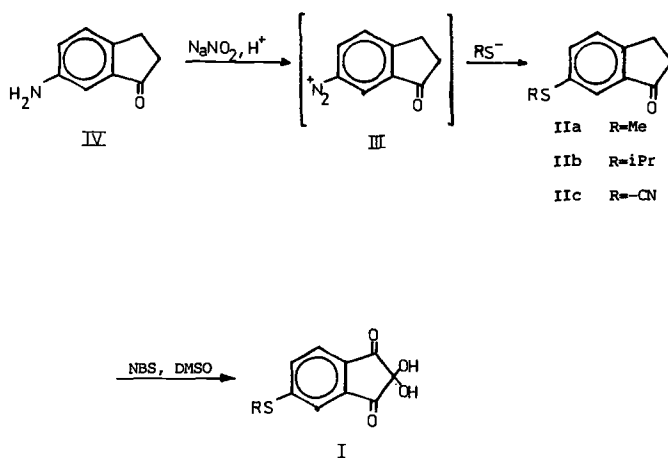


FIG. 1—A general synthetic pathway to 5-thioninhydrins.

the method suggested recently by Joullie et al.,³ starting from 4-methylthio benzaldehyde, a commercially available precursor containing the alkylthio group attached to the aromatic ring.

The 5-thiocyanate derivative (Ic) was prepared by a slightly different procedure. The diazonium salt (III) was reacted with potassium thiocyanate in the presence of a catalytic amount of CuI thiocyanate. The oxidation of the corresponding indanone (IIc) to ninhydrin was accomplished with selenium dioxide as the oxidizing reagent.

Spectral Data

Absorption spectra in solution were recorded on a GBC ultraviolet/vis 911 spectrophotometer (GBC Scientific Equipment, PTY Ltd., Victoria, Australia). Two light sources were used for luminescence excitation: the Quaser 30 xenon arc (Mason-Vactron, London) at the higher wavelengths (from 530 to 587 nm) and the Polilight xenon arc (Rofin, Australia) at the lower wavelengths (450 to 530 nm).

Fingerprint Samples

Latent fingerprint samples of various individuals were collected on four types of paper items: groundwood-free white paper, checks, Israeli banknotes, and \$1 U.S. bills.

The various reagents were always applied to latent fingerprints of a common donor, each finger being treated with a specific reagent.

Reaction with Alanine

Alanine was chosen as a model for amino acids. A few milligrams of the 5-substituted ninhydrin (I) were dissolved in a test tube containing approximately 2 mL of ethanol and

³Professor M. M. Joullie and her coworkers, working in cooperation with Dr. A. A. Cantu, U.S. Secret Service, have recently reported some very elegant synthetic routes to ninhydrin analogues, including two sulfur derivatives [12,13].

1% glacial acetic acid; alanine was added in slight excess, and the solution was boiled on a steam bath until the color remained unchanged (2 to 3 min). The solution was cooled to room temperature, diluted with ethanol, and the visible spectrum recorded. The sample was then divided into three test tubes. A few crystals of zinc acetate, cadmium iodide, and mercury bromide were added, the test tubes were gently shaken, and the spectrum recorded again. (Zinc acetate is less hygroscopic than zinc chloride and therefore preferable for the preparation of the reagent used in the spectrophotometric measurement. Data using zinc acetate were identical to those obtained using zinc chloride.)

Reaction with Latent Fingerprints on Paper Items

0.1% solutions of alkylthio ninhydrins (I) were prepared as follows: 50 mg of the compound were dissolved in a minimum amount of ethanol (2 to 3 mL) at room temperature. Acetic acid (0.5 mL) was added, and the solution was diluted with Freon 113 (fluorisol) to 50 mL. Latent fingerprints were developed by dipping, spraying, or swabbing with cotton-wool soaked in the solution. Items were heated for 2 to 3 min in a microwave oven in the presence of a beaker containing water. (Samples developed with DFO for comparison were heated for 20 min at 100° C.)

Results

All 5-thioninhydrins reacted with alanine to give colored products (Table 1). All developed latent fingerprints on paper to give purple images similar to those obtained with ninhydrin.

Treatment with zinc chloride changed the color to pink, both in solution and on paper. The images luminesced intensely upon illumination with the powerful light sources and observation through appropriate filters. (This is true for all types of paper that were examined, except for \$1 bills, where neither thioninhydrins nor DFO gave satisfactory results.)

Prints developed by this procedure luminesced much more intensely than ninhydrin-developed prints or even than prints developed with 5-methoxyninhydrin (V).⁴ Preliminary experiments showed that the detectability of latent fingerprints after treatment with 5-thioninhydrins (I) was equal to or better than that of DFO developed prints (Figs. 2,3).

The excitation range for the thioninhydrins-developed prints was quite wide. Fluorescence could be excited between 450 and 580 nm.

Cooling weak prints to liquid nitrogen temperature further enhanced the luminescence.

Discussion

5-Thioninhydrins are ninhydrin derivatives in which a divalent sulfur atom is directly attached to the carbon atom at position 5. They can be regarded as the sulfur analogues of 5-alkoxyninhydrins such as 5-methoxyninhydrin (V). Due to the lower electron affinity of the sulfur atom compared with oxygen and its ability to participate in charge transfer interactions with adjacent unsaturated systems, light absorption of sulfur compounds

⁴This reagent is regularly used by the laboratory in 0.2% solution in ethanol-freon 113, containing 1% acetic acid.

TABLE I—Solution spectral data: colors and absorption maxima before and after metal salt treatment.

Compound	Products with Alanine, Color and λ_{Maximum}	Color and λ_{Maximum} after Treatment with		
		Zn (II)	Cd (II)	Hg (II)
5-Methylthio ninhydrin (Ia)	blue, 417, 596	pink, 517	red, 408, 526	purple, 431, 550
5-Isopropylthio ninhydrin (Ib)	blue, 419, 595	pink, 518	red, 527	purple, 544
Ninhydrin-5-thiocyanate (Ic)	blue, 417, 586	orange, 421, 500	pink, 417, 515	pink-purple, 426, 534
Ninhydrin	blue, 408, 588	yellow, 486	pink, 410, 502	pink-purple, 415, 520
5-Methoxyninhydrin (V)	blue, 407, 588	orange, 497	pink, 407, 507	purple, 414, 531

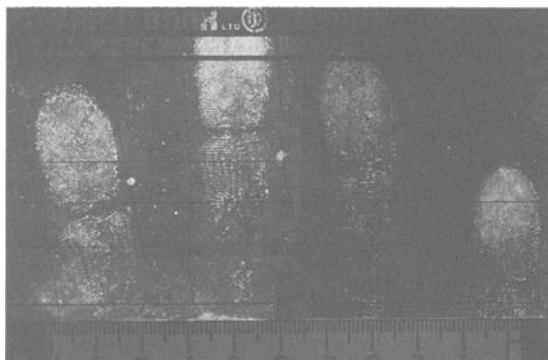


FIG. 2—Fluorescent impressions of latent fingerprints on a cheque after development with 5-methylthio ninhydrin (1a) (left half) and with DFO (right half). Excitation with Quaser 30 at 503 to 587 nm. Observation through a red filter (cut off at 593 nm).

occurs at longer wavelengths than their oxygen analogues [14]. This was the rationale behind the present study. Indeed, the reaction products of compounds (I) with amino acids and with latent fingerprints obeyed this rule (see Table 1).

As can be seen from Table 1, the thiocyanate derivative (Ic) is somewhat different from the two alkylthio derivatives (Ia, Ib). Its data are closer to those of the oxygen compound, 5-methoxyninhydrin (V). In our opinion, this is due to the strong electron-withdrawing effect of the cyano group on the sulfur, which reduces the availability of the sulfur electron pair and hence interferes with the charge transfer to the π system.

Our preliminary studies indicate that alkylthio ninhydrins (I) as fluorogenic fingerprint reagents are characterized by the following properties:

1. Both colored and fluorescent images are obtained, the former being an advantage over DFO.
2. Intense fluorescent images were produced (after secondary treatment with zinc chloride). The fluorescence compares favorably to that obtained with DFO and sometimes exceeds it.
3. A wide range of excitation.
4. Minimal background discoloration.
5. Convenient application (NFN formulation [15]).
6. Fluorescence enhanced upon cooling to liquid nitrogen temperature.

As a result, the study continues in two directions: (1) more sulfur derivatives will be synthesized and their properties examined and (2) attempts will be made to find optimal synthetic pathways to these intriguing compounds.

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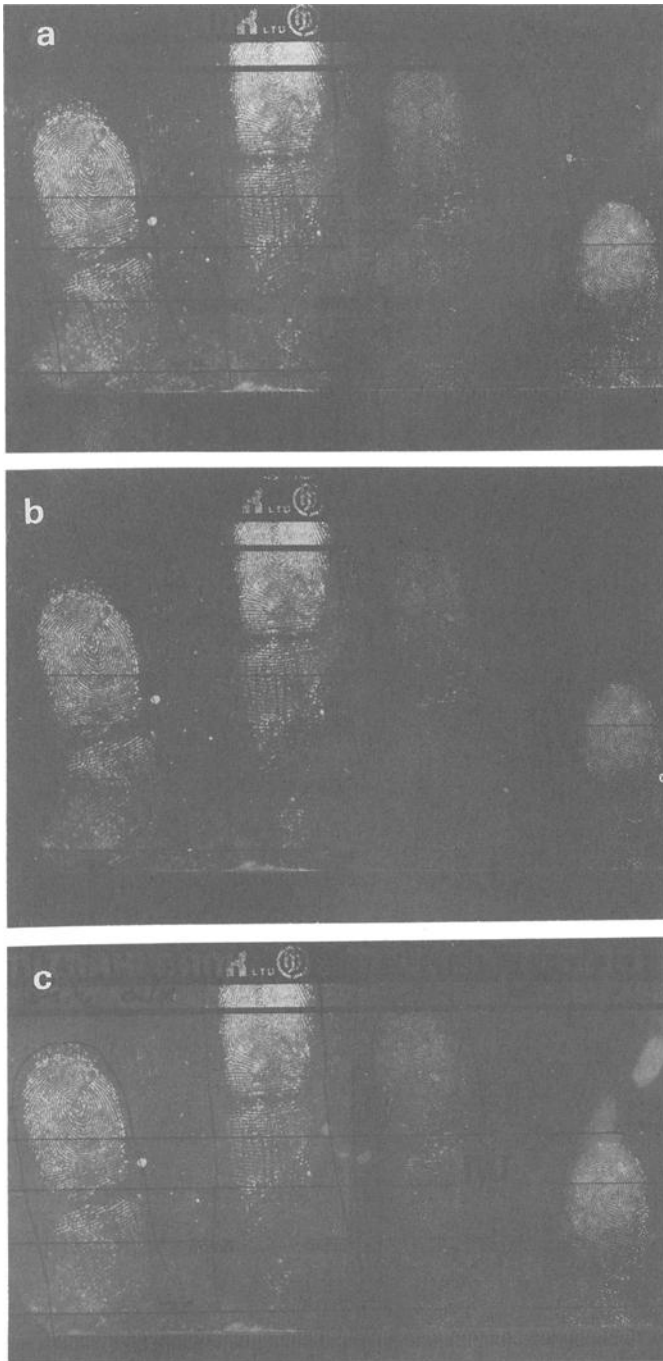


FIG. 3—Same fingerprints as in Fig. 2. Fluorescence excitation by Polilight: (a) Excitation at the 530-nm centered band. Observation through an orange filter (cut off at 549 nm); (b) Excitation at the 505-nm centered band. Observation through an orange filter (cut off at 515 nm); (c) Excitation at the 450-nm centered band. Observation through an orange filter (cut off at 529 nm).

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