TECHNICAL NOTE

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5-Methoxyninhydrin: A Reagent for the Chemical Development of Latent Fingerprints That is Compatible with the Copper-Vapor Laser

REFERENCE: Almog, J. and Hirshfeld, A., "**5-Methoxyninhydrin: A Reagent for the Chemical Development of Latent Fingerprints That is Compatible with the Copper-Vapor Laser,**" *Journal of Forensic Sciences,* JFSCA, Vol. 33, No. 4, July 1988, pp. 1027–1030.

ABSTRACT: 5-Methoxy-2.2-dihydroxy-1,3 indanedione (5-methoxyninhydrin), a relatively simple analogue of ninhydrin, exhibits excellent properties as a developer of latent fingerprints on paper. While visible development closely resembles that achieved with ninhydrin, fluorescence after zinc chloride treatment is considerably stronger than that of ninhydrin developed prints, particularly when excited by the green line of the copper-vapor laser.

KEYWORDS: criminalistics, fingerprints, 5-methyoxyninhydrin, lasers, latent fingerprints, copper-vapor lasers

Forensic science laboratories having access to a copper-vapor laser (CVL) are well aware that ninhydrin developed fingerprints treated with zinc chloride do not respond very well to the CVL. In general, only latent prints of "very good donors"[2] can be successfully visualized by CVL after ninhydrin-zinc chloride treatment. This is due to the fact that the complex of Ruhemann's purple (the product of ninhydrin and amino acids) and zinc chloride absorbs at about 490 nm (very close to the 488-nm line of the argon-ion laser; a very good excitation source for this complex) [*1*]. However, the gap of about 20 nm from the CVL's shortest line (510 nm) means that this chemical combination is not optimal for visualization of prints with the CVL.

The appearance of benzo[*f*]ninhydrin in 1982 [*2*] somewhat improved the situation for users of copper-vapor and other lasers. Latent fingerprints developed with this reagent and treated with zinc chloride fluoresce nicely when illuminated by the neodymium:yttrium aluminum garnet (Nd:YAG) laser, which has a line at 532 nm [*3*], or by the CVL [*4*]. Under

This is an expanded version of a presentation by one of us (J. A.) at the International Forensic Symposium on Latent Prints, Forensic Science Research and Training Center, FBI Academy, Quantico, VA, 7–10 July 1987. Received for publication 11 Sept. 1987; revised manuscript received 2 Nov. 1987; accepted for publication 13 Nov. 1987.

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[2]The "quality" of the "donors" is evaluated on the basis of the quality of their ninhydrin developed fingerprints (before zinc chloride treatment).

these conditions the prints fluoresce much more strongly than ninhydrin developed prints [3,4].[3] Because of this, and the dark green color it yields, benzo[*f*]ninhydrin became an operational fingerprint developer in a number of forensic science laboratories.

Benzo[*f*]ninhydrin, however, was not commercially available and even some of the starting materials for its synthesis disappeared from the market. Add to these difficulties the very high cost of production and it will become evident why we looked for other vicinal triketones as substitutes for benzo[*f*]ninhydrin.[4]

Out of a long list of such compounds which were synthesized and examined [2,5,6] we found that 5-methoxyninhydrin(I) not only met our expectations but markedly exceeded them. This relatively simple analogue of ninhydrin (recently mentioned by Warrener et al. [5]) is prepared in a single step from a commercially available material, 5-methoxy-1-indanone (II, Fig. 1). It develops latent fingerprints on paper in a similar fashion to ninhydrin: the same purple color is obtained (λ_{max} 582 nm) with about the same rate of development and sensitivity. After zinc chloride treatment of the surface, a noticeable difference between the two is observed when they are examined under the green line of the CVL. The 5-methoxyninhydrin developed prints (which absorb at λ_{max} 500 nm) emit a yellow fluorescence which is considerably stronger than the orange fluorescence emitted by ninhydrin developed fingerprints (Fig. 2). This fluorescence is so remarkable that it can be observed even without darkening the laboratory. Under these adverse conditions, even latent marks of very poor donors can be visualized.

Synthesis

5-Methoxy-1-indanone (II, Aldrich Chemical Co.), 550 mg (3.4 mmol) and selenium dioxide, 1.7 g (15.3 mmol) in dioxane (10 mL) were stirred under reflux for 6 h. After cooling, the solution was filtered and evaporated to dryness. The residue was chromatographed (thin-layer chromatography [TLC], silica plates, elution by dichloromethane: ethyl acetate 3:1). The main band ($R_f \sim 1/3$) was extracted (ethyl acetate). The residue after evaporation is a thick oil, 480 mg (68%), which can be used for fingerprint development without further purification. For characterization, a sample was chromatographed two more times to provide slightly yellow crystals, (from benzene: pet. ether 1:1), mp 80 to 85°C.[5] Electron impact (EI) mass spectrum includes a low abundant molecular ion (at *m/z* 190) and ions at *m/z* 162, 134 (base peak), and 106, corresponding to [M-CO], [M-2CO], and [M-3CO], respectively.

[3]A. A. Cantu, U.S. Secret Service, Washington, DC, personal communication, 1987.

[4]The Aldrich Chemical Co. has recently announced the availability of benzo[*f*]ninhydrin under the name 2,2-dihydroxy-1H-benz[*f*]indene-1,3(2H)-dione, Catalogue, No. 31,078-6, priced at $10.25 for 25 mg. A group at the University of Pennsylvania under Dr. Madeleine M. Joullié, working in conjunction with Dr. Antonio A. Cantu of the United States' Secret Service has developed a synthesis of benzo[*f*]ninhydrin using different starting chemicals and producing a higher yield than the techniques used previously.

[5]The melting point was not sharp as the compound could not be totally purified even after this procedure.

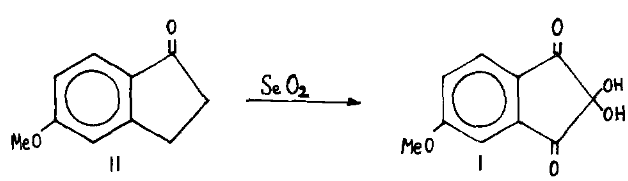

FIG. 1—*One-step synthesis of 5-methoxyninhydrin(I).*

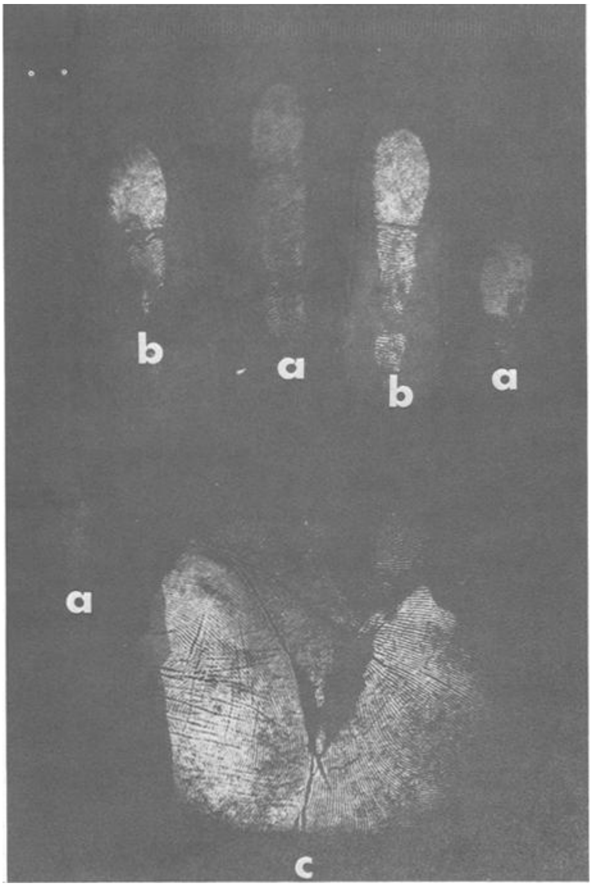

FIG. 2—*Fluorescent fingermarks of a "good donor"*[2] *examined under the green line of a CVL after development with ninhydrin followed by zinc chloride* (a) *benzo*[f]*ninhydrin followed by zinc chloride* (b), *and 5-methoxyninhydrin followed by zinc chloride* (c).

Fingerprint Development

A working solution contains 0.1% of the reagent (I) and 2% glacial acetic acid in ethanol. It can be applied by swabbing, spraying, or dipping.[6] The items are kept at room temperature for 24 h, steamed for 1 min, and sprayed with zinc chloride solution. The items are examined under the laser. An accelerated procedure involves the following steps: treatment with the reagent as above, steaming for 1 min, heating in the oven at 120°C for 1 min, steaming again for 1 min, zinc chloride treatment, and laser examination. Cooling the item to 77K (liquid nitrogen) for the laser examination [*5, 7, 8*] brings about a considerable enhancement of the fluorescence.

Results

This year 5-methoxyninhydrin was declared an operational reagent for fingerprint development in our laboratory. A blackmail letter that was treated with an ethanolic solution of

[6]A formulation based on fluorisol is now being used experimentally. These results will be reported along with other experience gained from casework in a full paper.

this reagent and subsequently with zinc chloride revealed a large number of fluorescent fingermarks under CVL illumination.

Recently, a rare opportunity was presented to compare the efficiency of this new reagent with that of ninhydrin under two different lasers (argon ion and copper-vapor) as well as three other light sources that have been reported in the literature (Dr. Terry Kent's "Quaser," manufactured by Mason-Vactron [7], the "Unilite" by Professor Warrener's group [8], and Dr. John Watkin's indium lamp [9]).[7]

Latent fingerprints were developed with ninhydrin or 5-methoxyninhydrin(I) followed by treatment with zinc chloride and examined under each of the five light sources. In all of these experiments, results for the prints developed with 5-methoxyninhydrin(I) were equal to or better than those developed with ninhydrin.

References

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[7]The three light sources were demonstrated by their inventors at an International Forensic Symposium on Latent Prints, Forensic Science Research and Training Center, FBI Academy, Quantico, VA, 7-10 July 1987.