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New Reagents for Development of Latent Fingerprints

A form of physical evidence always welcomed by prosecutors, fingerprints are unique records that can confirm the identity of a crime's perpetrator. Technically, fingerprinting is a biochemical method for determining the structure of a protein in which the protein is split into peptides by digestion with protease, and the fragments are separated in one direction by electrophoresis and at right angles by chromatography. After staining with a reagent, the peptide fragments are seen to be in characteristic locations. Improving the processes for obtaining usable prints as evidence has led to a search for superior development reagents to aid in identifying latent fingerprints. National Institute of Justice (NIJ)-sponsored research found ways to enhance the properties (e.g., line resolution, fluorescence) of one of the most commonly used reagents, ninhydrin, via structural modifications. In addition, ninhydrin analogs were altered to expand their solubility to a wider range of organic solvents.

Previous work on ninhydrin

Ninhydrin was first prepared in 1910 by the English chemist, Siegfried Ruhemann, who also investigated the formation of the violet compound (Ruhemann's Purple, or RP) produced by ninhydrin's reaction with amino acids.[1] The significance of this discovery to forensic science went unnoticed until 1954, when Oden and von Hoffsten reported the use of ninhydrin as a fingerprint developing reagent that reacts with amino acids secreted from sweat glands.[2] Although the content of amino acids in a fingerprint residue is low (compared to the content of salts and fatty acids), the RP produced from the reaction of these amino acids with ninhydrin is deeply colored, and the developed fingerprints are usually highly visible. Thus, ninhydrin has long been known as one of the most affordable and useful reagents for visualization of latent fingerprints on porous surfaces (such as paper, wood, and walls).

In cases where the developed fingerprints are weak, secondary treatment with an aqueous zinc chloride solution can improve the print's line resolution quality. Zinc chloride-treated prints can be observed as "glowing" (fluorescent) when illuminated with light of a certain wavelength. In 1990, C. A. Pounds and coworkers introduced the reagent 1, 8-diazafluorenone (DFO), which is commercially available and used in the United Kingdom.[3] Unlike ninhydrin, DFO gives a weakly colored initial print; the main feature of this reagent is its ability to give a fluorescent print without secondary treatment. However, some investigators currently report difficulties with uniform print development using DFO.

Synthesis of new ninhydrin analogs

The NIJ-sponsored research group had previously prepared a compound, thieno[f]ninhydrin, that provided an initial print as deeply colored as one produced with ninhydrin as the reagent.[4] Thieno[f]ninhydrin also displayed excellent fluorescent properties without requiring the use of a metal for secondary development. However, the organic compound was both difficult and expensive to produce on a commercial scale. Nevertheless, the new reagent indicated that the thienyl fragment could be one of the desirable structural features to incorporate into the ninhydrin molecule.

Until recently, protocols available for synthesis of ninhydrin analogs were inefficient. The research group reported novel approaches to the synthesis of benzo[f]-ninhydrin, 5-methoxy-ninhydrin, 5-(methylthio)ninhydrin, thieno[f]ninhydrin, as well as to the extended series of 5-phenyl- and 5-thienylninhydrin derivatives, starting from the inexpensive bromoxylene in a short high-yielding synthetic sequence. When tested, 5-(2-thienyl)ninhydrin and 5-(3-thienyl)ninhydrin (2-THIN and 3-THIN) displayed properties (i.e., brighter fluorescence, better line resolution) superior to ninhydrin's as fingerprint developing reagents.[5]

Chemical modifications facilitating the choice of solvent

Ninhydrin is commonly used for fingerprint development on porous surfaces, which are dipped in the reagent solution or sprayed with it. The choice of solvent is important—different kinds of inks on documents can be affected by the solvent employed; the fingerprint itself can be smeared by an inappropriate solvent. Solvents used in forensic science must pose no more than a minimal safety risk, in terms of properties such as flammability or toxicity, and they must also be environmentally safe. Chlorofluorocarbons, such as trichlorofifluoroethane, had been the solvents of choice in ninhydrin formulations. When banned recently by the Environmental Protection Agency, a search was begun for acceptable substitute solvents. In the ninhydrin study, researchers found that some derivatives of the reagent, resulting from its reaction with higher molecular weight or "long chain" alcohols (i.e., hemiacetals), undergo the same color-forming reactions as ninhydrin, but they are substantially more soluble in organic solvents (e.g., ethyl acetate, methylene chloride, or toluene). Hemiacetals can be quantitatively obtained from any ninhydrin analog in a one-step procedure.

Practical implications

Several synthetic approaches were developed and evaluated to provide a total of 21 new ninhydrin analogs. These reagents were evaluated for fingerprint visualization by forensic experts at the U.S. Secret Service and other law enforcement agencies, both in this country and in England, Switzerland, Australia, and Israel. The new methodology afforded two complementary reagents (2-THIN and 3-THIN), which displayed superior fingerprint developing properties. Large-scale production of 2-THIN has been initiated by Vinfer Ltd., a Northern Ireland manufacturer, to investigate its potential for commercialization.

This research has provided a viable solution to problems encountered by criminalists as a result of the prohibited use of chlorofluorocarbons.

Notes

1. Ruhemann, S., *Trans. Chem. Soc.*, 97 (1910):2025.

2. Oden, S. and B. von Hofsten, *Nature*, 173 (1954):449.

3. Pounds, C.A., R. Grigg, and T. Mongkolaussavaratana, *Journal of Forensic Sciences*, 35 (1990):169–175.

4. Cantu, A., D.A. Leben, M.M. Joullie, and R.R. Hark, *Journal of Forensic Identification*, 43 (1993):44–66.

5. Hark, R.R., D.B. Hauze, O. Petrovskaia, M.M. Joullie, R. Jaouhari, and P. McComiskey, *Tetrahedron Letters*, 35 (1994):7719–7722.

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