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Reagents for the Chemical Development of Latent Fingerprints: Synthesis and Properties of Some Ninhydrin Analogues

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ABSTRACT: In an attempt to design new reagents for the chemical development of latent fingerprints, a number of ninhydrin analogues were synthesized and their reactions with latent fingerprints on paper were studied. The ring-fused and substituted ninhydrins developed latent fingerprints with a sensitivity similar to that of ninhydrin. The most promising of the group was 2,2-dihydroxybenz[f]indane-1,3-dione, which developed latent fingerprints as dark green images with excellent resolution.

KEYWORDS: criminalistics, fingerprints, reagents, ninhydrin

It was recognized long ago that among the ingredients of palmar sweat amino acids are probably the most suitable substrates for the chemical development of latent fingerprints on porous surfaces [*1–3*]. It appears, however, that even ninhydrin (I), a universal reagent for the amino acids used in the development of latent fingerprints, was not developed on any theoretical basis but was instead discovered by coincidence. Its special reactivity with amino acids was postulated, in 1910, only after the discoverer, S. Ruhemann, had observed that the new compound stained the skin [*4*]. Ninhydrin was adopted for the detection of latent fingerprints on paper in 1954 [*5*] and since then has become the most common reagent for the chemical development of latent fingerprints. As ninhydrin formulations suffer from certain disadvantages [*1,6,7*], several groups of researchers have tried to modify them to improve their properties. The modifications involved variations in concentrations, solvents, and pH [*3*]. Some of these were very beneficial, such as the nonflammable ninhydrin formulation [*6,8,9*].

We thought that a different approach to latent fingerprint development could be a chemical modification of the ninhydrin molecule itself. To the best of our knowledge such an experiment has never been done before in forensic chemistry. The idea seemed even more encouraging after we read the following paragraph, which Professor Rubin wrote in 1975 [*10*]:

> There is no reason, a priori, why other triketones should not react with amino acids in a manner analogous to ninhydrin. In fact, colored products ... have been observed in reactions with benzoninhydrins.

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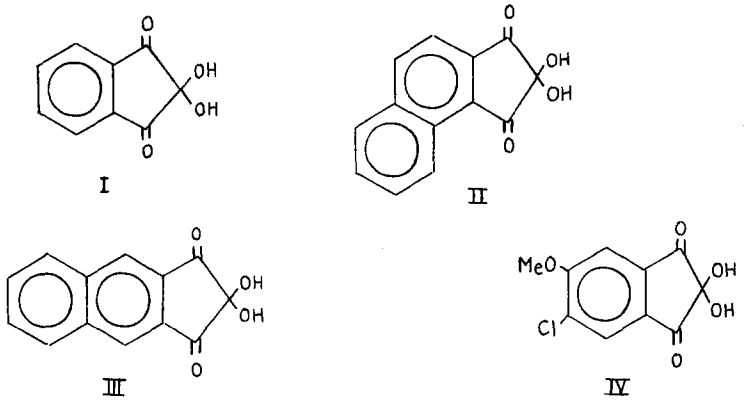
Thus, we prepared the two benzoninhydrins, 2,2-dihydroxybenz[e]indane-1,3-dione (II) and 2,2-dihydroxybenz[f]indane-1,3-dione (III), and the substituted ninhydrin, 2,2-dihydroxy-5-chloro-6-methoxyindane-1,3-dione (IV) (Fig. 1), and examined their reactions with latent fingerprints on paper.

Method

The substituted and ring-fused ninhydrins (VII, Fig. 2) were prepared by adopting the method suggested by Becker [*11*] for the synthesis of unsubstituted ninhydrin. The starting materials were the corresponding dimethyl esters (V), which were reacted with dimethyl sulfoxide in the presence of sodium methoxide (Fig. 2). The intermediate compounds (VI) were not purified and no attempts were made to optimize the yields.

Latent fingerprints were collected from different persons on a commonly used white groundwood-free paper. Three fingerprints from each hand were developed, each one by a different ninhydrin analogue (Compounds II to IV). A fourth fingerprint was developed by ninhydrin for comparison (Fig. 3). The reagents were applied to the latent prints by gently



I 2,2-dihydroxy-1,3-indanedione (ninhydrin)
II 2,2-dihydroxybenz[e]indane-1,3-dione (benzo[e]ninhydrin)
III 2,2-dihydroxybenz[f]indane-1,3-dione (benzo[f]ninhydrin)
IV 2,2-dihydroxy-5-chloro-6-methoxyindane-1,3-dione

FIG. 1—*Ninhydrin and some analogues.*

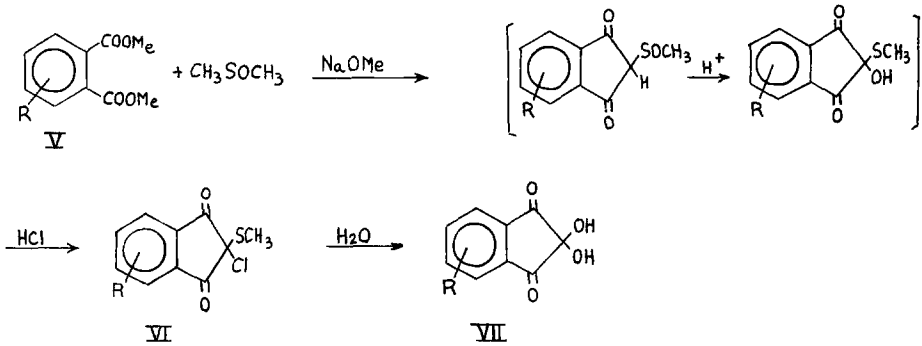


FIG. 2—*Becker's method* [11] *as adopted for the synthesis of substituted and ring-fused ninhydrin.*

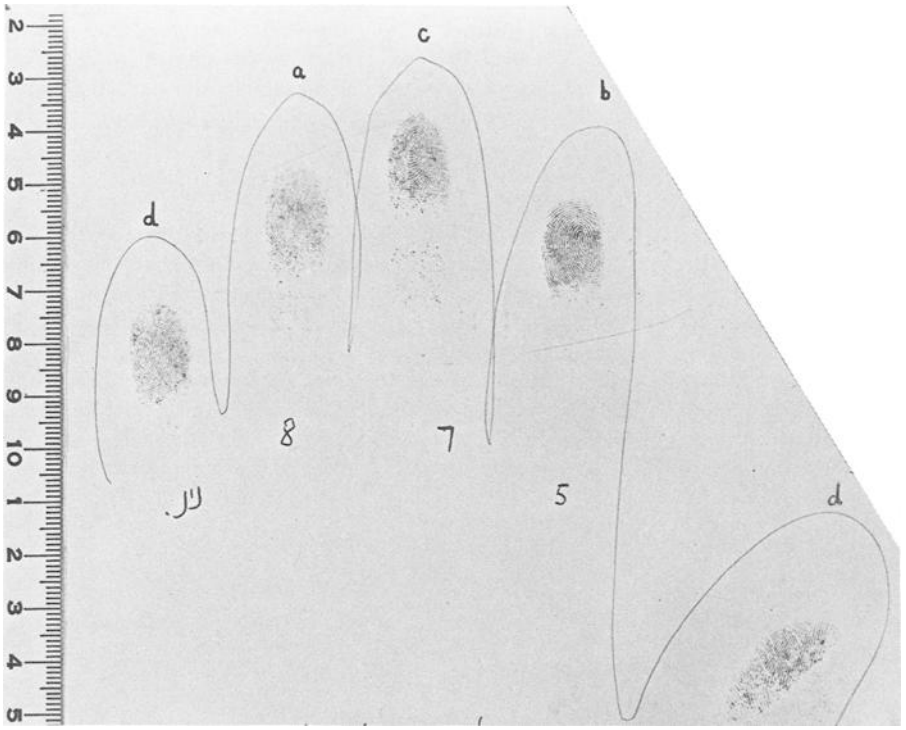


FIG. 3—*Impressions of six-week-old latent fingerprints from a good donor obtained with the ninhydrin analogues:* (a) *Compound II;* (b) *Compound III;* (c) *Compound IV; and* (d) *ninhydrin.*

swabbing the paper with a cotton wool swab soaked with a 1% methanolic solution of the compound containing a trace of glacial acetic acid. The prints were then developed either at room temperature or in a dry oven (120°C) for 2 min.

2,2-Dihydroxybenz[f]indane-1,3-dione (III) was prepared according to Jones and Wife [*12*] from dimethyl naphthalene-2,3-dicarboxylate [*13*] and dimethyl sulfoxide.

2,2-Dihydroxybenz[e]indane-1,3-dione (II) was prepared on a 10-mmole scale by the same method [*12*] from dimethyl naphthalene-1,2-dicarboxylate [*13*] and dimethyl sulfoxide. The product (II) had the same physical properties as 2,2-dihydroxybenz[e]indane-1,3-dione prepared earlier by a different method [*13*].

2,2-Dihydroxy-5-chloro-6-methoxyindane-1,3-dione (IV) was prepared by the same method [*12*] from dimethyl 3-chloro-4-methoxyphthalate (Fig. 2, Compound V, R = 3-chloro-4-methoxy-). It was fully characterized by its mass spectrum and by nuclear magnetic resonance, infrared, and ultraviolet spectroscopy. Full details will be reported shortly.

Results

Reactivity

Fresh solutions of all three ninhydrin analogues (II to IV) developed latent prints on paper with a sensitivity similar to that of ninhydrin. Sensitivity was judged by the fingerprint technicians and was based on visual impressions of a large number of fingerprints from the same person. The quality of the fingerprint donors was assessed by the quality of their ninhydrin-developed latent fingerprints, and the analogues gave excellent results with latent prints taken from good donors while poor impressions were formed from fingerprints from poor donors.

Rate of Reaction

The ring-fused ninhydrin (III) reacted at the same speed as ninhydrin both at room temperature and in the oven (colors reached maximum intensity at the same time). The substituted ninhydrin (IV) did not react as quickly under the same conditions, and the second benzoninhydrin (II) was the slowest to react (about twice the time for complete development).

Color

Latent fingerprints that were developed by the substituted ninhydrin (IV) came out as purple impressions, very similar to the Ruhemann's purple obtained with ninhydrin. The ring-fused ninhydrins, on the other hand, gave different colors: benzo[e]ninhydrin (II) gave pink impressions while benzo[f]ninhydrin (III) gave blue-green impressions, with very good contrast and resolution.

For a more definite color characterization all four compounds were reacted in solution with the amino acid alanine (1% solution in methanol, boiled for 1 min) and the visible spectra of the solutions were recorded after cooling. Data are listed in Table 1.

Age

Latent fingerprints were examined at ages from a few minutes to six weeks. The quality of the development was found to be age-independent and old fingerprints came out as well as fresh ones with all four reagents.

Background Discoloration

A faint background discoloration of the same color as the developed prints was observed in all the experiments, ninhydrin included. This effect was stronger when development was accelerated by heat.

Image Stability

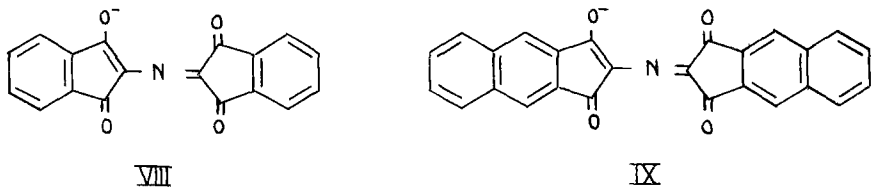
The visible impressions developed by all four compounds were stable for at least a few months. On a few of the prints the blue-green impressions obtained with Compound III slowly changed to dark purple, retaining the good resolution.

Discussion

The present theory of the mechanism of the reaction between ninydrin and amino acids specifies at least five consecutive stages [*14*]. It was therefore difficult to assume exactly how a certain alteration of the ninhydrin molecule would affect the reaction of the compound with amino acids. It seemed logical, however, to try such modifications as would lead to pro-

TABLE 1—*Absorption maxima of the reaction mixtures of ninhydrin analogues and alanine (1% methanolic solution) (Cary 15 spectrophotometer).*

Compound	λ_{max}, Absorption in nm		
I (ninhydrin)	404		582
II	406	497	
III	429		629, 644
IV	408		580



VIII IX

FIG. 4—*Ruhemann's purple (VIII), the final product of the ninhydrin reaction with amino acids* [14] *and the assumed product of the benzoninhydrin (III) with amino acids (IX).*

ducts having the longer conjugated systems (Fig. 4) that are expected to show stronger absorption of light [*13*] with maximum absorption at longer wavelengths [*15*] (bathochromic shift) as compared with Ruhemann's purple. The two benzoninhydrins (II and III) were therefore the first candidates for preparation and examination.

Substituents on the aromatic ring, because of their electronic effects, might also affect the physicochemical properties of the compound. Attempts to prepare ninhydrin analogues bearing strong electron-withdrawing substituents such as nitro or dichloro were not particularly successful. Using the 3- and 4-nitrophthalates (V) (R = 3-NO_2 and 4-NO_2, respectively) as starting materials gave highly colored products of unidentified structure while dimethyl 3,4-dichlorophthalate (V), (R = 3,4-di-chloro) under the strong basic conditions of the reaction gave the desired product, 2,2-dihydroxy-5,6-dichloroindane-1,3-dione (VII) (R = 5,6-di-chloro) only in very low yield, the major product being 2,2-dihydroxy-5-chloro-6-methoxyindane-1,3-dione (IV). The latter compound (IV) was then prepared by an unambiguous route from dimethyl 3-chloro-4-methoxyphthalate (V) (R = 3-chloro-4-methoxy).

As expected, the three ninhydrin analogues were found to be quite efficient developers of fingerprints.

The close similarity of the developing properties of ninhydrin and the substituted ninhydrin (IV) can be attributed to the structural proximity (the combination of chloro and methoxy substituents on the aromatic ring in Compound IV, on the basis of their electronic effects, is not expected to vary the chemical properties a great deal).

The dark green product of benzo[f]ninhydrin (III) with amino acids and with latent fingerprints represents a considerable bathochromic shift compared with Ruhemann's purple. However, it is too early to ascribe the green color to Structure IX because the product has not been isolated and characterized.

In conclusion, while the sensitivity of the new reagents for detecting latent fingerprints is not greater than that of ninhydrin, this study has nevertheless clearly shown that they can be designed and prepared by a stepwise modification of known reagents. In addition, we have recently obtained positive results in a similar study on the chemical modification of another fingerprint reagent, orthophthaladehyde [*16*]. That study will be reported shortly.

From an operational point of view, 2,2-dihydroxybenz[f]indane-1,3-dione (III) shows the greatest potential as a reagent and we are studying its possible advantages over ninhydrin, particularly its use on colored papers and for photographing the resulting images.

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