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Reagents for Chemical Development of Latent Fingerprints: Vicinal Triketones—Their Reaction with Amino Acids and with Latent Fingerprints on Paper

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ABSTRACT: Eleven vicinal triketones and one vicinal tetraketone were reacted with amino acids in solution and with latent fingerprints on paper. All cyclic triketones gave colored products with amino acids in solution and developed latent fingerprints on paper. The products' colors varied depending on the structure of the triketone. The potential of these compounds as fingerprint developers is discussed.

KEYWORDS: criminalistics, fingerprints, paper, reagents

Ninhydrin (2,2-dihydroxy-1,3-indanedione) is undoubtedly the most important reagent for chemical development of latent fingerprints on paper. Its reaction with amino acids present in palmar secretions brings about the formation of a colored product, Ruhemann's purple, which forms a visual image of the ridge detail. A few years ago it was shown that not only ninhydrin, but also its analogues that maintain its functional group (the vicinal triketone[2]) intact, react with amino acids in the same manner as ninhydrin and will also develop latent fingerprints on paper [*1*].

The rate of reaction and the products' colors were found to depend on the chemical structure of the ninhydrin analogue. Later it was found that the addition of Group IIb metal salts to the colored products forms fluorescent complexes which may enhance the detectability of the latent prints [*2*].

This article reports the study of a few more vicinal triketones, both ninhydrin analogues and others, as well as their reactions with amino acids and with latent fingerprints on paper. Vicinal triketones that were studied (Table 1) belong to the following groups:

(1) ninhydrin and ring fused (conjugated) ninhydrins,
(2) substituted ninhydrins,
(3) other ring systems involving a vicinal triketone (alicyclic and heterocyclic[3]), and
(4) open chained vicinal polyketones.

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[2]Although they are referred to as triketones, many of these compounds form hydrates quite readily and the gem-dihydroxy structure has generally been accepted as their correct presentation [*3*].

[3]Three of the heterocyclic triketones (X-XII) were not tested by this group and data concerning them are from the literature.

TABLE 1—*Vicinal triketones that were studied throughout this work.*[2,3]

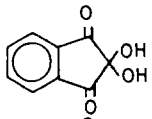
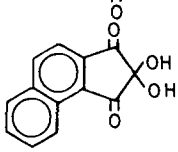
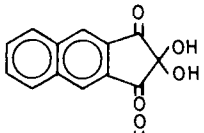
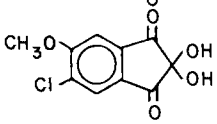
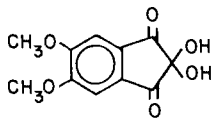
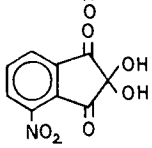
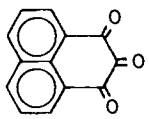
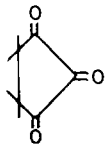
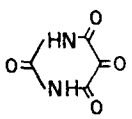
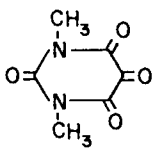
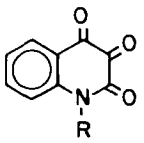
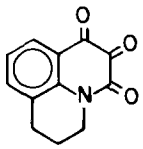
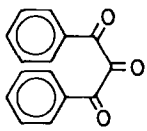
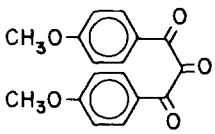
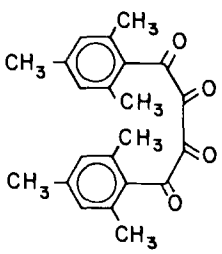
Compound	Chemical Structure	Name
I		ninhydrin
II		benzo(*e*)ninhydrin
III		benzo(*f*)ninhydrin
IV		5-chloro-6-methoxyninhydrin
V		5,6-dimethoxyninhydrin
VI		4-nitroninhydrin
VII		2H,3H-dihydrophenalene-1,2,3-trione
VIII		4,4,5,5-tetramethylcyclopentanetrione
IX		alloxan
X		1,3-dimethylalloxan

TABLE 1—(*Continued*).

Compound	Chemical Structure	Name
XI		quinisatin (and *N*-substituted derivatives)
XII		1,8-trimethylenequinisatin
XIII		1,3-diphenylpropane-trione
XIV		1,3-*di*-(4-methoxyphenyl)-propanetrione
XV		1,4-*di*-(2,4,6-trimethylphenyl)-butanetetrone

Method

Materials

Ninhydrin (I), AR, was purchased from Merck Co., Darmstadt (W. Germany). The two ring fused ninhydrins (II, III) and chloromethoxyninhydrin (IV) were previously described by this group [*1*].

5,6-Dimethoxyninhydrin (V) was prepared according to Kametani et al. [*4*] by hydrolyzing the condensation product between dimethoxyindanone and *N,N*-dimethyl-*p*-nitrosoaniline in hydrochloric acid 18%. The isolation stage was slightly modified: the crude dimethoxyninhydrin was extracted by ten consecutive portions of chloroform. After evaporation, treatment with water, and recrystallization from water, a pure product (V) was

obtained (56% yield). This compound had the following properties: melting point 257 to 258°C[4]; mass spectrometry (MS) *m/z* 220 (M+), 192 (M-CO), 164 (M-2CO), 136 (M-3CO); hydrogen-nuclear magnetic resonance (H^1-NMR) (CD_3COCHD_2) 4.06 (S, 6H), 4.57 (d, $\mathcal{J}$ = 3.44 Hz, 2H = 2 geminal hydroxyls on carbon 2), 7.37 (S, 2H); and infrared analysis (IR) (KBr) 870, 1078, 1243, 1508, 1574, 1703, 1745, and 3148 cm^{-1}.

4-Nitroninhydrin (VI) was prepared according to Prikule and Neiland [5] by hydrolysis of the betaine obtained from 4-nitroindanedione and iodosobenzene diacetate.

Samples of dihydrophenalene trione (VII), tetramethylcyclopentane trione (VIII), diphenylpropane trione (XIII), *di*-(4-methoxyphenyl)-propanetrione (XIV), and *di*-(trimethylphenyl)-butanetetrone (XV) were kindly provided to us by Professor Mordecai B. Rubin of the Chemistry Department, Technion—Israel Institute of Technology, Haifa, Israel (for full description of these compounds see Ref *6*).

Alloxan (IX), AR, was purchased from Sigma Chemical Company, St. Louis (U.S.A.).

Dimethylalloxan (X), quinisatin (XI), and trimethylenequinisatin (XII) were not tested by us, and the data concerning their reaction with amino acids are from the chemical literature (Table 2).

Fingerprint Samples

Latent fingerprint samples of two individuals, a good donor and an average one (as determined by the quality of their ninhydrin developed prints), were collected on groundwood-free white paper. Samples were kept at room temperature and developed at intervals from one day to two months.

Reaction with Amino Acids in Solution

Alanine and glycine served as model compounds. Small amounts of amino acids were dissolved in ethanol containing 1% glacial acetic acid. Triketone was added (approximately

TABLE 2—*Colors and absorption maxima of the reaction mixtures of cyclic vicinal triketones with amino acids and with latent fingerprints on paper.*

Compound	Color	λ max, nm
I	purple	404, 582
II	pink	406, 567
III	dark green	429, 630
IV	purple	408, 580
V	purple	406, 523 (in neutral solution the maxima are 405 and 580 nm)
VI	purple	409, 580 (in neutral solution the maxima are 405 and 599 nm)
VII	blue-purple	425
VIII	red	582
X	red-blue purple	530 [*7-9*]
XI	not specified	not specified [*10*]
XII	blue [*11*]	not specified

[4]The melting point of (V) is considerably higher than the one reported by Kametani et al. for the same compound [*4*] (214 to 217°C). The analytical data of our compound, however, are in very good agreement with the structure of (V).

2.5 equimolar amounts) and the solution was boiled on a steam bath until the color remained unchanged (5 to 15 min). The solution was cooled to room temperature, diluted with ethanol, and the visible spectrum was recorded (for reasons of solubility, benzo(*f*)ninhydrin (III) and nitroninhydrin (VI) were dissolved in dioxane:methanol 1:1 instead).

Reaction with Latent Fingerprints on Paper

Ethanolic solutions, 1 to 2%, of the triketones also containing 1% glacial acetic acid were applied to the latent prints by gently swabbing the paper with a cotton-wool swab soaked in the solution. The prints were then allowed to develop at room temperature. (Benzo(*f*)ninhydrin (III) and nitroninhydrin (VI) were applied in dioxane:methanol 1:1 solution instead.)

Results

Reactivity

All *cyclic* vicinal triketones (Compounds I to XII) reacted with amino acids to give colored products (data regarding Compounds X to XII are based solely on the literature [*7-11*]) (Table 2).

All *cyclic* vicinal triketones (Compounds I to IX) developed latent fingerprints on paper. (The heterocyclic triketones, X-XII, were not tested in this experiment.)

The quality of the developed prints, as judged by our fingerprint laboratory experts, had the following order:

$$\text{I} \sim \text{III} > \text{V} > \text{II} \sim \text{IV} \sim \text{IX} > \text{VI}$$

Ninhydrin (I) and benzo(*f*)ninhydrin (III) gave results of similar quality, which were slightly better than those obtained with dimethoxyninhydrin (V). Benzo(*e*)ninhydrin (II), chloromethoxyninhydrin (IV), and alloxan (IX) gave results of similar quality, which were less satisfactory than the previous ones. In this group, nitroninhydrin (VI) gave the least satisfactory development, mainly as a result of contrast problems. Dihydrophenalene trione (VII) developed latent prints quite nicely; the ridge details appeared in blue-purple with good contrast, but further testing is still required with this compound.

While most cyclic triketones reacted more or less at the same rate as ninhydrin, 4-nitroninhydrin (VI) was definitely the fastest, both with amino acids in solution and with latent fingerprints on paper. The color change upon reaction with alanine or glycine was instant and the solution turned dark purple during the addition of (VI) to the amino acid at room temperature. Latent fingerprints became visible a few seconds after being treated with (VI).

Color

The resultant colors are dependent on the various chemical structures of the triketones (Table 2). While the reaction products of all ninhydrin related triketones (I-VI) exhibited two absorption maxima in the visible spectrum, products of the other cyclic triketones (VII-XII) exhibited only one absorption maximum in that domain (the products derived from dimethoxyninhydrin (V) and nitroninhydrin (VI) showed a considerable pH dependence as well).

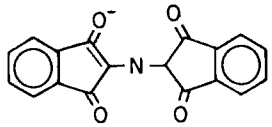
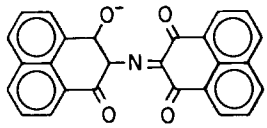
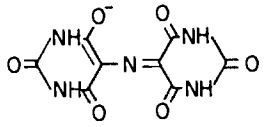
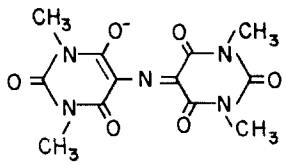
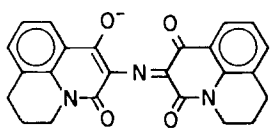
In the development of latent fingerprints on paper, background discoloration was noticeable with most triketones, excluding ninhydrin. However, while background color was relatively weak with benzo(*f*)ninhydrin (III), in the case of 4-nitroninhydrin (VI) it significantly reduced the contrast, thus reducing the detectability of the latent prints.

Discussion

In a previous paper it was shown that fingerprint reagents related to ninhydrin could be designed and prepared [*1*]. Studies with an analogous series of such compounds was required to indicate some directions for future research and development and particularly for tailoring reagents for specific requirements. In the present study an attempt was made to look at factors such as conjugation, substituents, and ring size and to compare cyclic and noncyclic systems.

Perhaps the most obvious observation of this study was that only cyclic triketones produced colors with amino acids, while the open chained triketones did not give colored reactions with amino acids or with latent fingerprints. A possible explanation for this clear distinction might be the conformational difference between the two types: while the cyclic triketones are planar, or nearly planar, the stable conformation of the open chained triketones is a noncoplanar one, with dihedral angles of 180 and 90° between the carbonyl groups [*6,12*].

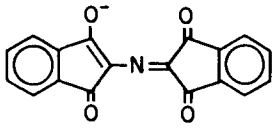
TABLE 3—*Some known analogues of Ruhemann's purple and their precursors.*

Compound (Precursor)	Ruhemann's Purple Analogue	Ref
I		*13*
VII		
IX		*7-9*
X		*7-9*
XII		*11*

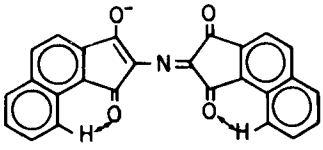
There is a strong basis to ascribe a Ruhemann's purple-type structure to the colored products of the above reactions (although it has not been proven in all cases, a number of such compounds which were prepared by the same manner have been described in the literature [Table 3], and their structures unambiguously determined). The central moiety of all these compounds is essentially identical. It must have a planar or nearly planar configuration; otherwise these substances remained colorless because resonance would be inhibited [*14*].[5] This may explain why open chained triketones may not be potential fingerprint reagents.

Deviation from planarity might also explain the hypsochromic effect of the additional fused ring in (II) as compared with ninhydrin (I). The steric interaction between the protons at Position 4 and the carbonyl groups (Fig. 1) may twist each half of the molecule from a planar configuration, thus lessening the resonance and the color [*6,14*]. On the other hand, the second isomer with an additional conjugated ring, benzo(*f*)ninhydrin (III), is devoid of such interactions, hence the additional ring contributes mainly to the reduction of the resonance energy which is expressed in deepening the color (bathochromic effect).

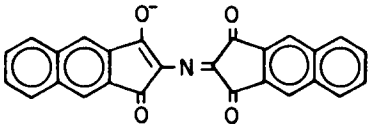
Substituents on the aromatic ring apparently have a smaller effect on the color. The number of substituted ninhydrins studied in this work was too small to draw solid conclusions, but it seems that electron attracting groups such as nitro may contribute to a bathochromic



XVI



XVII



XVIII

FIG. 1—*Ruhemann's purple analogues derived from ninhydrin (XVI), benzo*(e)*ninhydrin (XVII), and benzo*(f)*ninhydrin (XVIII). The arrows mark the possibility of steric interactions between the protons on the carbon at Position 4 and the carbonyl oxygens in (XVII).*

[5]In a recent paper by Grigg et al. [*15*], the crystal structure of Ruhemann's purple is reported. While each half of the molecule is planar, there is an angle of about 20° between the two halves as a result of the repulsion between two adjacent carbonyl groups.

effect and electron donating groups such as methoxy may contribute to a hypsochromic effect.

It is felt that at this stage it is too early to refer to ring size and its overall effect. It is clear, however, that not only five membered ring triketones (such as ninhydrin and its analogues), but also six membered rings such as the alicyclic dihydrophenalene trione (VII) and the heterocyclic alloxan (IX), give colored products with amino acids and develop latent fingerprints on paper. In fact, alloxan (IX) was previously suggested as a potential fingerprint reagent [*16*] and studied in depth by this group. Under no circumstances was it found comparable with ninhydrin in its fingerprint developing properties [*17*].

Going from color development to fluorescence by addition of metal salts may add another dimension to the search for fingerprint developers. With the recent introduction of new light sources, fingerprint development may in many cases become a problem of matching a triketone with an appropriate metal salt and with the available light source (initial experiments with these compounds and metal salts, using a copper vapor laser as excitation source are encouraging and will be reported in a forthcoming paper). The question of availability will remain, of course, as most of the vicinal triketones are not commercial substances. A possible solution might be access to a decent organic chemistry laboratory. The more promising compounds may become available on the market upon demand.

Acknowledgment

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The author also wishes to thank Professor M. B. Rubin of the Chemistry Department, Technion—Israel Institute of Technology, Haifa, Israel, for kindly providing samples of the open chained triketones and compounds (VII) and (VIII).

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