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Latent Fingerprint Visualization by 1,2-Indanedione and Related Compounds: Preliminary Results

REFERENCE: Almog J, Springer E, Wiesner S, Frank A, Khodzhaev O, Lidor R, Bahar E, Varkony H, Dayan S, Rozen S. Latent fingerprint visualization by 1,2-indanedione and related compounds: preliminary results. J Forensic Sci 1999;44(1): 114–118.

ABSTRACT: A number of vicinal cyclic diketones, most of them belonging to the 1,2-indanedione series, have been prepared and tested as potential reagents for latent fingerprint development. Unsubstituted 1,2-indanedione and a number of its mono- and dimethoxy- derivatives exhibited excellent properties as fluorogenic reagents for latent prints on paper. Structural modifications, such as substitutions at position 3, omission of the benzene ring or increase of the five-membered to a six-membered ring, considerably reduced this activity. Quite surprisingly, benzo[f]indane-1,2-dione, which was synthesized for the first time in this work, was significantly inferior to 1,2-indanedione as a fingerprint reagent.

Even at this stage, before optimization of the reaction conditions, it can be said that some 1,2-indanediones are at least as sensitive as DFO. Their solubility in nonpolar solvents and relative ease of preparation are further advantages. It is the authors' opinion that 1,2-indanedione itself may soon become a practical fingerprint reagent.

KEYWORDS: forensic science, cyclic diketones, 1,8-diazofluorene-9-one, latent fingerprints, fluorescence, indanediones

In 1990, Pounds, Grigg, and Mongkolaussavaratana published their discovery that 1,8-diazofluorene-9-one (DFO), a compound closely related to the active moiety of ninhydrin, gave a strong fluorogenic reaction with latent fingerprints on paper (1). Since then, DFO has become the main fluorogenic reagent for developing latent fingerprints on paper in many forensic science laboratories (2,3). But, even DFO suffers from some deficiencies such as high cost and low solubility in nonpolar solvents. In addition, due to ecological considerations, much research has been carried out over the past few years into finding substitutes for CFC solvents such as Freon 113. No substitute solvent has been found to compare with Freon 113 in the preparation of DFO solutions (4). It has, therefore, become important to find other reagents that can compete with DFO in fingerprint development.

Last year, Joullie, Cantu and their co-workers (5) discovered that 1,2-indanedione (compound 1) and some of its derivatives can also visualize latent fingerprints by a direct fluorogenic reaction. One derivative, 5,6-dimethoxy-1,2-indanedione (compound 5) was found to be more amino-acid sensitive than DFO (5,6) and also had other advantages over DFO such as higher solubility and lower cost (6).

In order to investigate some of the structural requirements of the 1,2-indanedione reaction and perhaps combine color development with fluorogenic activity, we have prepared a series of such compounds (Table 1, compounds 1–11) and also some other cyclic α-diketones (Table 1, compounds 12–16) and studied their reaction with latent fingerprints on paper.

For some 1,2-indanediones that could not be synthesized by the method described by Cava (7), we devised a novel synthetic route, using the $HOF{\cdot}CH_3CN$ complex as the oxidizing agent (8). The structural modifications in the 1,2-indanedione molecule involved substitutions of the aromatic ring (Table 1, compounds 2–6), substitutions at position 3 (Table 1, compounds 7–10), an additional benzene ring (Table 1, compound 11), omission of the benzene ring (Table 1, compounds 12, 13), ring enlargement (Table 1, compound 14), and two other vicinal cyclic diketones that are not directly related to 1,2-indanedione (Table 1, compounds 15, 16). The fluorogenic reaction with latent fingerprints was found to be most pronounced in the indanedione series. Development conditions were 100°C at 60% relative humidity for 30 min. The reagent 1,2-indanedione and its mono- and dimethoxy- derivatives developed fluorescent fingerprint impressions whose brightness matched or exceeded that of DFO. Development conditions for DFO were dry oven at 100°C for 20 min. No great differences were found among the unsubstituted and the mono- and dimethoxy-indanediones, although the fluorescence (and background) of the dimethoxy-indandione was slightly brighter. In these experiments, methanol was tested as the solvent for the vicinal diketones and Freon, as the major solvent for DFO. Solutions of 0.01% of the vicinal diketones

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Received 18 Feb. 1998; and in revised form 27 April 1998; accepted 27 April 1998.

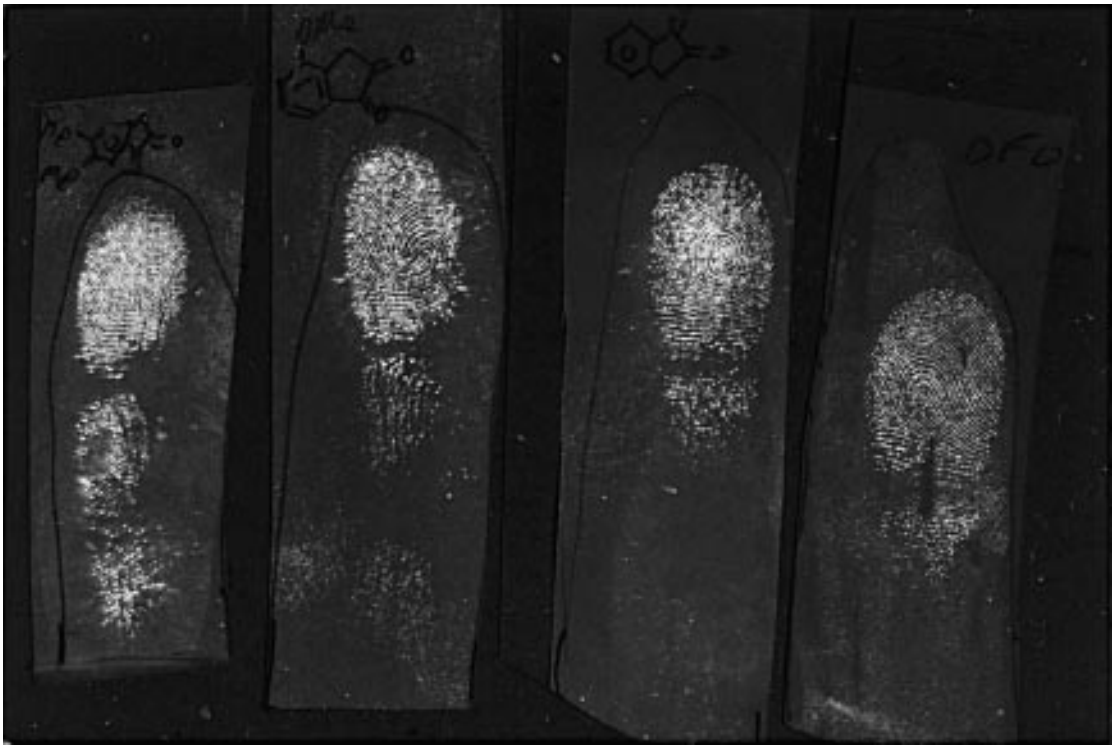


FIG. 1—*Prints developed with, from left to right: 5,6-dimethoxy-1,2-indanedione, 4-methoxy-1,2-indanedione, 1,2-indanedione, and DFO. Indanedione's solution concentration 0.01%, DFO concentration, 0.025%, excited at 530 nm and viewed through 550 nm cut-off filter.*

in acidified methanol gave optimal results (maximum visibility of latent prints and minimum background noise (Table 4)). Less polar solvents are currently under investigation. For instance, initial experiments with the solvent Vertrel XF (4) are very promising.

Experimental

1,2-Indanediones were generally prepared according to Cava (7) from the corresponding 1-indanones in a two-step synthesis (compounds 1–6, 8, 9). 1,2-indanediones that could not be obtained by this procedure were prepared by oxidizing the corresponding 1-indanones with the $HOF{\cdot}CH_3CN$ complex and further oxidation with Jones reagent, the α-hydroxyindanones thus formed (compounds 7 and 11) (8).

Compounds 8–10 and 12–14 were prepared according to procedures reported in the literature (Table 1).

Squaric acid (compound 15) was purchased from Aldrich Chemical Co. Diazaphenanthroquinone (compound 16) was obtained from Teva Pharmaceutical Industries (Israel).

Each dione was dissolved in 10 mL of methanol and a drop (0.05 mL) of acetic acid. The solutions were initially prepared at reagent concentrations of 0.25% (w/vol). The Freon-based DFO reagent used throughout the experiment was prepared in accordance with the Manual of Fingerprint Development Techniques (2) (with 3% by volume methanol and 2% acetic acid) at a concentration of 0.025%.

Various individuals placed prints of both hands on white A4/80 gram photocopy paper. The paper was cut into individual ''fingers'' and each piece of paper was sprayed with a different solution. The DFO-treated paper was placed in a dry oven at 100°C for 20 min (optimal conditions for DFO development). The other papers were placed for 30 min in a humidity cabinet at 100°C and 60% relative humidity (not necessarily the optimal conditions, but preliminary tests showed that these conditions gave good results). The developed fresh fingerprints were then illuminated with a Rofin Polilight at 530 nm and viewed through an orange 549 nm cutoff filter (not necessarily the optimal conditions for all of the reagents). The fluorescence was graded ''+'' to ''+++'' judged by the fluorescence intensity of the fingerprints. Fluorescing prints that looked at least as good as the fluorescence of DFO were given a rating of ''+++''. Attention was also given to the color and background of the fingerprints while observing them in white light and also to the background fluorescence. This process was repeated for reagent concentrations of 0.05%, 0.01% and 0.0004%. Fingerprints were further treated with $ZnCl_2$ and the fluorescence was again observed.

Results and Discussion

The experimental results are displayed in Tables 2 to 5. Unsubstituted 1,2-indanedione (compound 1) and its mono- and dimethoxy- derivatives (compounds 2–5) were found to be very good fluorogenic reagents for latent fingerprints. Their sensitivity is at least as good as that of DFO (Fig. 1). Substitutions at position 3 (compounds 7–10) considerably reduce this effect. Also, omission of the benzene ring (compounds 12, 13) or modification of the five-membered ring to a six-membered ring (compound 14), has the same detrimental effect. The two cyclic diketones that are not related to indanedione (compounds 15, 16) showed very little activity (1,8-diazaphenanthro-9,10-quinone) or none at all (squaric

acid). In all cases, further treatment with $ZnCl_2$ did not appreciably affect the fluorescence.

Qualitative experiments showed that 1,2-indanedione and most of its analogs dissolve much better in nonpolar solvents, such as petroleum ether, Freon 113, and Vertrel XF, than does DFO (preliminary experiments were also carried out by a group from the BKA and a group from the University of Lausanne-IPSC and were presented at the First European Meeting of Forensic Science in Lausanne in 1997).

It should be noted that while in casework, one may develop additional fingerprints with ninhydrin after using DFO, this was not the case when sequencing the 1,2-indanedione and then ninhydrin. This may be the result of a more complete reaction of the 1,2-indanedione with the amino acids as compared to DFO.

Fusion of a second benzene ring (compound 11) did not bring about the expected color-deepening effect. This was somewhat surprising in light of the color enhancement and red-shift that was observed with the same modification in the ninhydrin series (14). The 5-fluoro- derivative (compound 6) also exhibited a fluorogenic effect as the other indanediones but the fluorescence was weaker.

None of the cyclic diones (1–16) gave any remarkable color reaction with latent fingerprints. The faint colors that developed with some of the new reagents were negligible as compared to the fluorescence.

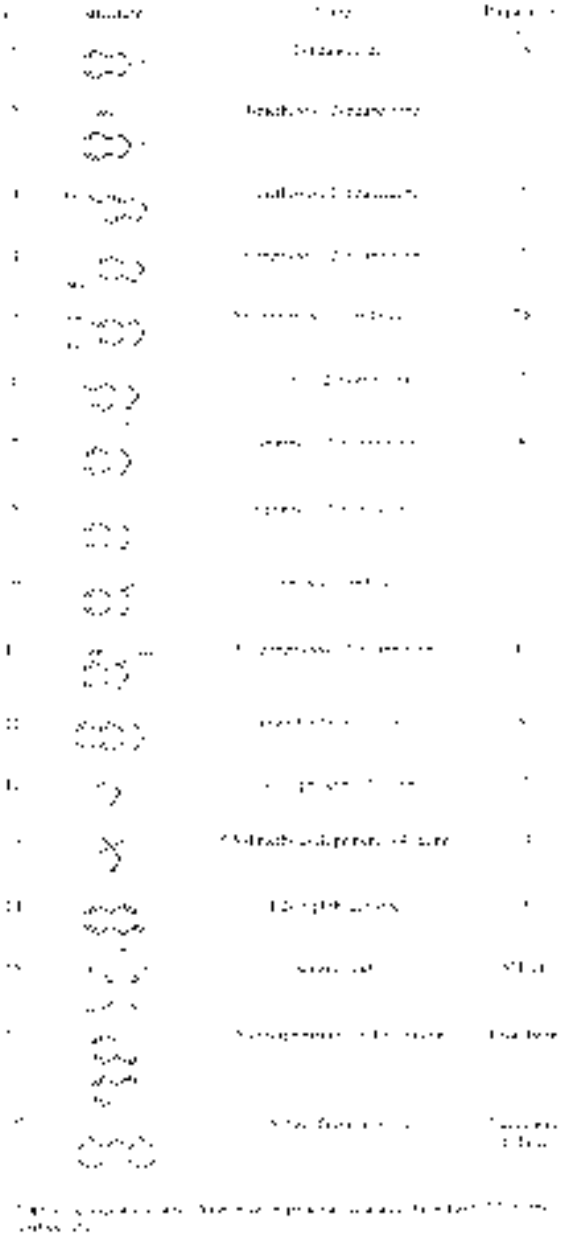
At higher reagent concentrations (0.25% and 0.05%), for the paper used, some background color and fluorescence developed (except for 1,2-indanedione). Moreover, the background of color and fluorescence disappeared when the concentration was reduced to 0.01%, without affecting the fingerprint development (Table 4).

All five indanediones in Table 4 gave similar chromogenic and fluorogenic results to those observed with DFO. Although the fingerprint fluorescence of dimethoxy-indanedione was slightly stronger than the fluorescence of the other indanediones (excluding the experiment performed at the lowest reagent concentration), the same was true for the background fluorescence. If one considers also the cost, then a formulation which is based on 1,2-indanedione (1) should be significantly less expensive than both the other indanediones (compounds 2–5) and DFO.[5]

There are three apparent points of discrepancy between our results and those reported by Joullié et al. (who tested the reagents on glycine) (5,6). First, while we did not find an appreciable difference between diones 1–5, they found that the dimethoxy derivative (compound 5) was much more sensitive. Second, while we found that the 5-fluoro derivative did give a noticeable fluorescence with fingerprints, they did not observe any fluorescence. And third, in our experiments, the $ZnCl_2$ treatment did not consistently enhance the fluorescence. One must, however, keep in mind that different testing methods were used by each group.

The reaction mechanism between indanediones and perspiration ingredients is still under investigation (M. M. Joullié, personal communication). We feel it is too early to speculate on mechanistic considerations. When the mechanism is fully understood, it may be possible to reconcile the above differences. It is assumed that amino acids are the main substrates for the indanediones reactivity; however, reaction with other residual components cannot be ruled out. Such a reaction, along with the fact that each group employed different testing methods, could reconcile, in part, the apparent discrepancies.

TABLE 1—*Vicinal dyketones tested in present work.*



Conclusion

Preliminary experiments indicate that 1,2-indanedione may become a useful latent fingerprint reagent in the near future. In no way was it found to be inferior to DFO. The main problem associated with its use is its present availability, but it is not difficult to synthesize. The scope and limitations, including parameters such as shelf life and optimum developing conditions, still remain to be clarified. Synthesis of large quantities has started and it seems that 1,2-indanedione will be much less expensive than other fluorogenic reagents. Ease of preparation, solubility in nonpolar solvents and, above all, sensitivity, render it a good candidate to become a part of the fingerprint development arsenal.

[5] The substituted 1-indanones which are the starting materials for the 1,2-indanediones are much more expensive than 1-indanone itself. Initial scaling-up experiments indicate that 1,2-indanedione (1), which is not commercially available at present, may be prepared for much less than the present price of DFO.

TABLE 2—*Vicinal diketones—results at 0.25% concentration.*

Number	Reagent	Fingerprint Color	Background Color	Fingerprint Fluorescence	Background Fluorescence
1	1,2-indanedione	faint pink	none	+ + + yellow	+
2	4-methoxy-1,2-indanedione	faint pink	light yellow	+ + + yellow	+
3	5-methoxy-1,2-indanedione	faint pink	light yellow	+ + + yellow	+
4	6-methoxy-1,2-indanedione	faint pink	light yellow	+ + + orange	+
5	5,6-dimethoxy-1,2-indanedione	faint pink	dark yellow	+ + + orange	+
6	5-fluoro-1,2-indanedione*	none	orange	+ +	none
7	3-methyl-1,2-indanedione*	faint purple	yellow	+	+
8	3-phenyl-1,2-indanedione	none	none	+ + yellow	none
9	3,3-dimethyl-1,2-indanedione	none	none	+ orange	none
10	3,3-dimethoxy-1,2-indanedione	faint purple	none	none	none
11	benzo(f)indane-1,2-dione*	none	orange	+	+
12	1-cyclopentene-3,4-dione	none	brown	none	+
13	5,5-dimethyl cyclopentene-3,4-dione	none	orange	+ yellow	+
14	-1,2-naphthoquinone	none	brown	+ yellow	+
15	squaric acid	none	none	none	none
16	1,8-diazaphenanthro-1,2-quinone	none	green	+ yellow	none
17	DFO†	faint pink	none	+ + + orange	none

* These reagents were first dissolved in a minimal amount of methanol, but the main carrier was CFC113.
† DFO is not part of the series, is Freon-based, is of concentration 0.025%, and requires dry heat to react.

TABLE 3—*Indanedione and analogs—results at 0.05% concentration.*

Number	Reagent	Fingerprint Color	Background Color	Fingerprint Fluorescence	Background Fluorescence
1	1,2-indanedione	faint pink	none	+ + + yellow	none
2	4-methoxy-1,2-indanedione	very faint pink	very faint yellow	+ + + yellow	none
3	5-methoxy-1,2-indanedione	none	very faint yellow	+ + + yellow	none
4	6-methoxy-1,2-indanedione	pink	very faint yellow	+ + + orange	+
5	5,6-dimethoxy-1,2-indanedione	faint pink	yellow	+ + + orange	+
8	3-phenyl-1,2-indanedione	none	none	+ yellow	none

TABLE 4—*Indanedione and analogs—results at 0.01% concentration.*

Number	Reagent	Fingerprint Color	Background Color	Fingerprint Fluorescence	Background Fluorescence
1	1,2-indanedione (1)	none	none	yellow + + +	none
2	4-methoxy-1,2-indanedione (2)	none	none	yellow + + +	none
3	5-methoxy-1,2-indanedione (3)	none	none	yellow + + +	none
4	6-methoxy-1,2-indanedione (4)	none	none	yellow + + +	none
5	5,6-dimethoxy-1,2-indanedione (5)	none	none	orange + + +	slight

TABLE 5—*Indanedione and analogs—results at 0.0004% concentration.*

Number	Reagent	Fingerprint Color	Background Color	Fingerprint Fluorescence	Background Fluorescence
1	1,2-indanedione (1)	none	none	+ +	none
2	4-methoxy-1,2-indanedione (2)	none	none	+ +	none
3	5-methoxy-1,2-indanedione (3)	none	none	+	none
4	6-methoxy-1,2-indanedione (4)	none	none	+	none
5	5,6-dimethoxy-1,2-indanedione (5)	none	none	+	none

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