Monatshefte für Chemie - Chemical Monthly
https://doi.org/10.1007/s00706-018-2260-5

ORIGINAL PAPER

Amino acid-sensitive reagents with coumarin moiety for latent prints examination

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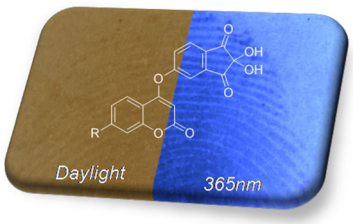
Received: 5 April 2018 / Accepted: 19 June 2018

Abstract

New ninhydrin derivatives were designed for the development of latent fingerprints on paper surfaces. The target compounds combine the selectivity of an amino acid-sensitive reagent with the variability of spectral characteristics of a fluorescent probe. These ninhydrin analogues, 2,2-dihydroxy-5-(2-oxo-2*H*-chromen-4-yloxy)-2*H*-indane-1,3-diones, prepared by multistep synthesis show enhanced fluorogenic properties compared with the commonly used ninhydrin. These types of derivatives can be potentially used for development of the latent prints on the dark surfaces, because their ninhydrin reaction products provide fluorescent prints under the UV light. The prints developed using these compounds are stable, visible and do not vanish from paper for a relatively long time (5 months).

Graphical abstract



Keywords Amino acids · Dual fingerprint reagent · Heterocycles · Ninhydrin · Nucleophilic substitutions

Introduction

Ninhydrin (2,2-dihydroxyindane-1,3-dione, **1**) has been widely used in many fields of chemistry, biochemistry, and forensic science since its synthesis by Ruhemann [1]. The broad application of **1** (Fig. 1) results from its reactivity towards a plethora of substrates. The most extensively studied and publicised have become the colour-forming reactions with amines and amino acids leading to the non-fluorescent Ruhemann's purple (**2**) [2–6].

Bodily fluids assembled in latent (invisible) fingerprints on porous or non-porous surfaces and on a large variety of materials are the most common type of evidence found at the crime scenes and the most problematic, whereas they require the enhancement methods to reach visible and recordable fingerprints. Of considerable interest are

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00706-018-2260-5) contains supplementary material, which is available to authorized users.

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Published online: 27 August 2018

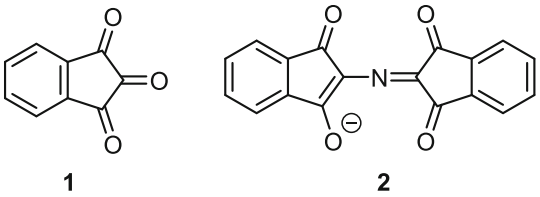


Fig. 1 Structure of ninhydrin (**1**) and Ruhemann's purple (**2**)

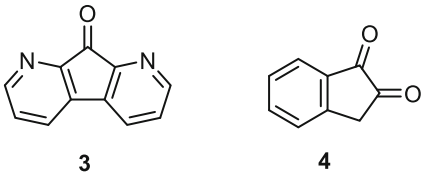


Fig. 2 Structure of 1,8-diazafluoren-9-one (**3**, DFO) and 1,2-indanedione (**4**)

chemical techniques for visualisation of latent prints on paper and related cellulosic materials, since our society relies on such materials for official documents, packaging, and currency printing. The introduction of ninhydrin (**1**) as an affordable and easily applicable chemical reagent for visualisation of the amino acids present in latent fingerprints on porous surfaces has revolutionised approaches to forensic examinations [2, 4, 6].

Due to their high stability, amino acids are the most desirable components of latent fingerprints on paper. Since amino acids have a high affinity for cellulose, the main component of paper, they do not bleed from paper's surface and the concentration in fingerprints does not vary in time as in the case of uric acid or inorganic salts, for instance. The main advantage of ninhydrin (**1**) lies in its ability to visualise latent fingerprints with low concentration of amino acids, corresponding to a content of about 250 ng per print, on paper [3, 6]. The ninhydrin reaction provides a product with a high molar extinction coefficient under very mild reaction conditions. The introduction of various substituents and the extension of the conjugated system of the ninhydrin skeleton, while preserving the reactivity of cyclic triketone, cause an increase in molar extinction coefficients yielding more sensitive reagents and inducing shifts of absorption maxima, resulting in some variation in the colour of the Ruhemann's purple products [3]. However, fingerprint experts are still trying to resolve the problem of the lack of contrast and sensitivity observed in particular on coloured surfaces. The Ruhemann's purple (**2**) forms a coordination complex with a metal salt (e.g. zinc chloride) which results in a colour change. Additionally, the complex shows intense fluorescence viewed under argon laser [7–9]. On reducing the temperature, the intensity of fluorescence enhances significantly [7].

An ideal dual fingerprint reagent is expected to produce both coloured and fluorescent impressions in a single reaction with latent fingerprint. 1,8-Diazafluoren-9-one (**3**, DFO, Fig. 2), undoubtedly the most significant fluorogenic fingerprint reagent to date, can be considered as a dual reagent, but the pink colour it produces with latent fingerprints is very faint and insufficient for the detection of most latent prints. DFO impressions are actually detected only by their fluorescence [4, 10, 11]. A similar behaviour is exhibited by a more recent reagent, 1,2-indanedione (**4**), which also produces colourless to faint pink impressions with latent fingerprints (also known as the Joullié's pink) that fluoresce in the visible domain [12–14]. As a result, compound **4** is regarded as the most sensitive of all commonly used reagents; however, **1** is the most widely used due to the cost and intense initial colour [13].

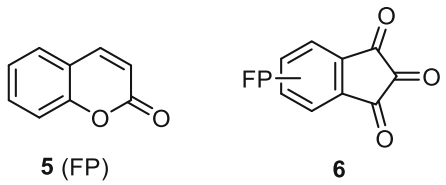
Although fluorescence detection is a common practice in fingerprint development now, in the available literature there are not lots of published reports dealing with the idea of linking ninhydrin (**1**) and some of the known fluorescent probes to a single molecule. We report a synthesis of a new type of ninhydrin analogue which combines the selectivity of the amino acid-sensitive reagent with the variability of the spectral characteristics of a fluorescent probe. A coumarin skeleton was chosen as the fluorescent probe. Its derivatives are known for their spectral properties, mainly the intense fluorescence observed in many derivatives with appropriate substitution as they are important components of functional molecules (e.g. probes, sensors, switches, and molecular devices) [15–17].

Despite the fact that more than 90 ninhydrin derivatives and analogues have been reported in literature [2–5], synthesis of a new type of ninhydrin derivatives with enhanced fluorogenic and chromogenic properties is still of high interest.

Results and discussion

Design and synthesis of a novel ninhydrin analogue

Previously examined approaches concerning modification of the structure of **1** have not led to any widely applicable dual ninhydrin fingerprint reagent [2–9]. When proposing the new reagent structure, it was necessary to fulfil the requirement of preserving the cyclic triketone part of ninhydrin (**1**) to ensure the reactivity with the amino acids in latent fingerprints. Having experience with the synthesis and study of the spectral properties of coumarin (**5**) and its derivatives [18–22], we have decided to link these two substructures into molecule **6** (Fig. 3). In spite of a possible applicability of the combined moieties, only one report in literature concerning the combination of coumarin and



5 (FP) **6**

Fig. 3 Structure of coumarin (**5**, FP - fluorescent probe) and ninhydrin-coumarin derivative (**6**)

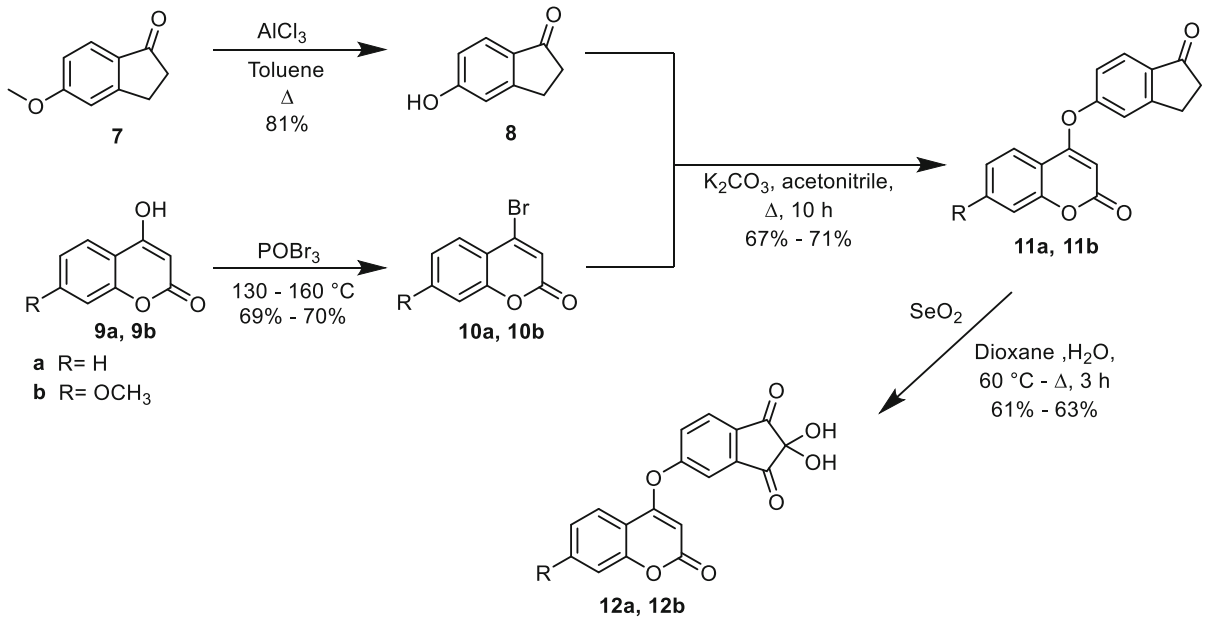
ninhydrin skeletons into one molecule has been published, although without preserving the triketone function [23].

We hoped to find a reagent that would react with fingerprint amino acids within 4 h to afford a molecule exhibiting sufficiently different absorption and fluorescence characteristics compared to those of the reagent (e.g. a change in the position of the absorption and emission maxima, a change of the extinction coefficients, a change of the quantum yield of fluorescence or the lifetime of the fluorescence emission). The formation of a product in which absorption and emission maxima are significantly redshifted (bathochromically) as a consequence of a more intense intramolecular charge transfer could lead to an elimination of background fluorescence. The increase of the signal/noise ratio results in a significant augmentation of the contrast between the developed fingerprint and the surface. Various non-covalent interactions (e.g. electrostatic interactions, hydrogen bonds) might also contribute to the increase of the contrast between visualised fingerprints and paper surface. The proposed molecules should also have a higher sensitivity than the ones only using the detection of colour change.

A concise, multistep synthesis was designed to afford new ninhydrin derivatives. The two above-mentioned moieties were linked through an *O*-bridge (Scheme 1).

Commercially available 5-methoxyindanone (**7**) was dealkylated using $AlCl_3$ to afford the indanone **8** in good yield [24]. The coumarin substructures suitable for linking with 5-hydroxyindanone (**8**) were prepared by facile bromination of 4-hydroxycoumarins **9** with $POBr_3$ to give 4-bromocoumarins **10** in acceptable yields. As coumarins **5** substituted with good leaving groups in position 4 of the skeleton are very useful substrates for coupling and nucleophilic substitution reactions [25, 26], we carried out the nucleophilic reaction of coumarins **9** with indanone **8**. This reaction in dry acetonitrile in the presence of K_2CO_3 under reflux led to coumarin derivatives **10** in 67–71% yields. The isolation of products was simple due to their precipitation after the addition of ice to the reaction mixtures. All other components of the reaction mixtures remained in the acetonitrile/water mixture. Simple purification of 4-(1-oxo-2,3-dihydro-1*H*-inden-5-yloxy)-2*H*-chromen-2-ones (**11**) by crystallisation from appropriate solvent (ethanol or *n*-heptane) is an additional benefit. Contrary to the reaction in acetonitrile, the same reaction performed in dry acetone or dry dichloromethane did not lead to the desired products; only starting materials and traces of products (< 5%) were obtained in those cases, possibly because of a worse transition state solvation.

Scheme 1



Coumarins **11** can be readily oxidised to ninhydrin derivatives **12** by SeO_2 in dioxane. The addition of water (5%) to the reaction mixture improved the yields of the products. We obtained two new derivatives **12** in good yields (61–63%) as stable hydrates. A formation of dihydroxy derivatives was expected, since it is generally known that ninhydrin exists as a stable hydrate and the tricarbonyl form is only present under rigorously anhydrous conditions [1]. Applying reaction conditions reported by Joullié [2] to the oxidation of indanone derivatives to ninhydrins in acetic acid/dioxane mixture or in glacial acetic acid did not lead to an increase of yields of products, and tarry by-products only separable by chromatography were formed in addition to the desired ninhydrins **12**.

Behaviour of prepared ninhydrins

Fluorescence spectroscopy was used for monitoring the spectral behaviour of ninhydrin derivatives **12** in methanol and chloroform. The fluorescence of coumarin derivatives depends on the substitution of the coumarin skeleton (**5**). We have observed a different structural character for the fluorescence spectra of the prepared ninhydrins **12**. Ninhydrin **12a** (unsubstituted phenyl ring in the coumarin scaffold) has an emission maximum at 376 nm in $CHCl_3$ and at 388 nm in MeOH. A substitution with an electron-donating group (OMe) leads to an intramolecular charge transfer in the compound **12b** affecting the formation of the new batochromically shifted band caused by a new deactivation path in the de-excitation process (Fig. 4). Thus, the spectrum of the methoxy derivative **12b** exhibits two emission maxima in chloroform, one just like **12a** at 376 nm and the second one at 453 nm.

Furthermore, the methoxy derivative **12b** fluoresces more intensively due to the electron-donating substituent bound in the position C-7 of the coumarin skeleton compared to the unsubstituted **12a**. The intensity of fluorescence depends on the solvent polarity; however, it has only slight influence on the position of the emission maxima. The ratio of band's intensity I_{453}/I_{376} for **12b** is larger than 1 in chloroform; this applies vice versa to methanol (Fig. 4).

As mentioned above, the structure of compounds **12** was designed to improve the quality of fingerprint impressions by the enhancement of the contrast between a background and the developed fingerprint itself. We have assumed that the fluorescence of ninhydrin reaction products obtained by reaction of **12** with the amino acids presented in latent fingerprints contributes to the quality improvement of the fingerprint impressions without another secondary treatment. Therefore, we have examined the reactivity of ninhydrins **12** with amino acids. We have monitored the influence of the amino acid phenylalanine on the fluorescence of **12** in solutions under conditions simulating some real circumstances of the fingerprint development process (Figs. 5, 6).

As can be seen in Figs. 5 and 6, a significant increase of fluorescence intensity occurs after the addition of the amino acid to ninhydrins **12** solutions. The largest change in the fluorescence intensity is achieved after heating the solutions with phenylalanine for 3 min in both cases. This behaviour of prepared derivatives **12** fulfils the fundamental objective of using fluorescence to increase the quality of visualised fingerprints. The heating treatment corresponds with a commonly used ninhydrin latent print enhancement procedure in forensic laboratories.

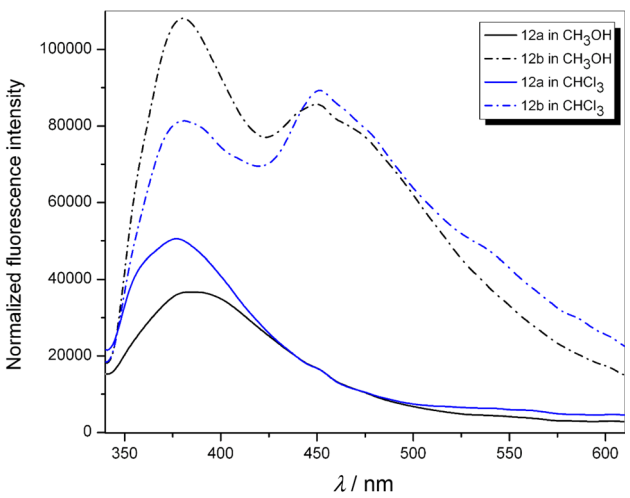


Fig. 4 Emission spectra of compounds **12** in methanol and chloroform ($c = 5 \times 10^{-5}$ M, $\lambda_{ex} = 320$ nm)

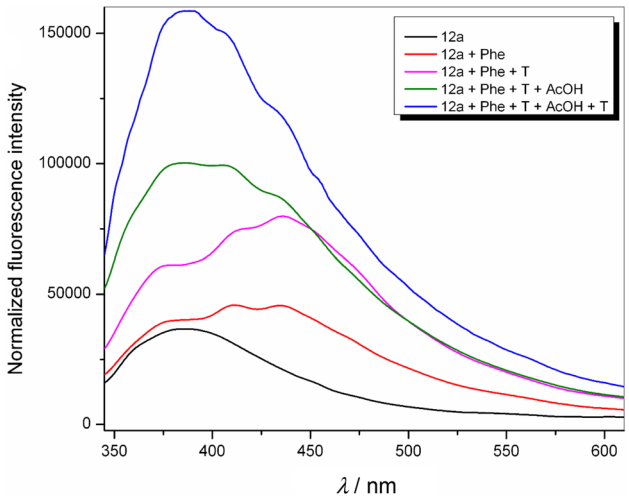


Fig. 5 Emission spectra of **12a** in methanol in the presence of 0.5 eq phenylalanine and glacial acetic acid ($c_{\mathbf{12a}} = 5 \times 10^{-5}$ M, $\lambda_{ex} = 320$ nm, $T = 50$ °C for 3 min)

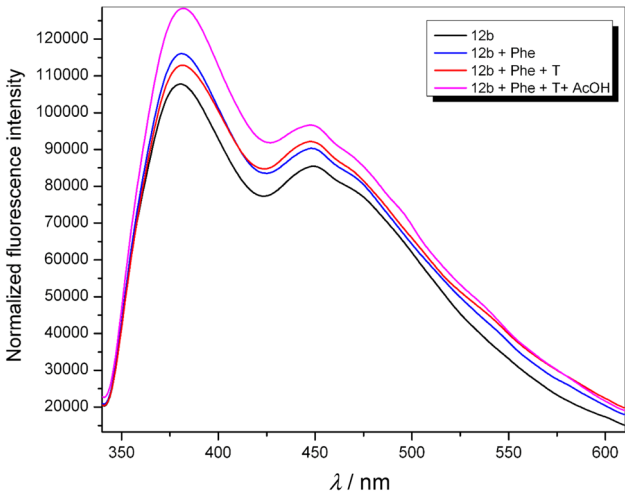


Fig. 6 Emission spectra of **12b** in methanol in the presence of 0.5 eq phenylalanine and glacial acetic acid ($c_{\mathbf{12b}} = 5 \times 10^{-5}$ M, λ_{ex} = 320 nm, T = 50 °C for 3 min)

Fingerprint development

The detection of a latent fingerprint can be done in many ways, although some are purely theoretical and unusable in forensic practice. On the other hand, there is no method which is known to be universal and applicable for all materials or conditions; therefore, the usage of each method varies from case to case.

To test the efficiency of the prepared compounds **12a** and **12b** for the latent fingerprint enhancement, we prepared a reagent solution. Latent fingerprints were collected on a white paper (the standard copy paper, 80 g/m^2) from donors who had not consumed food or handled chemicals 30 min prior to providing specimen fingerprints. Brown-red fingerprints were developed in 5 min. Figures 7 and 8 show comparisons of the developed fingerprints in daylight as well as with a 365 nm light source.

Compounds **12** provide fingerprint impressions with improved contrast between the developed fingerprint and the background. The developed fingerprints are visible in daylight; moreover, the change of wavelength to 365 nm results in improved and clear fingerprints suitable for fingerprint identification. This fact is consistent with the measured fluorescent spectra of the prepared compounds.

These types of the derivatives are potentially suitable for the development of latent prints on dark surfaces, since ninhydrin reaction products produce fluorescent prints under UV light. The prints developed using these compounds are stable and do not vanish from paper for a relatively long time (5 months).

Conclusion

New ninhydrin derivatives were designed and successfully synthesised by a good yielding, multistep protocol. These compounds can be used as dual fingerprint reagents. 2,2-Dihydroxy-5-(2-oxo-2*H*-chromen-4-yloxy)-2*H*-indane-1,3-diones produce highly coloured Ruhemann's purple species that also exhibit fluorescence without secondary metal treatment. The usage of these compounds could simplify the visualisation of latent fingerprints and may benefit the forensic community.

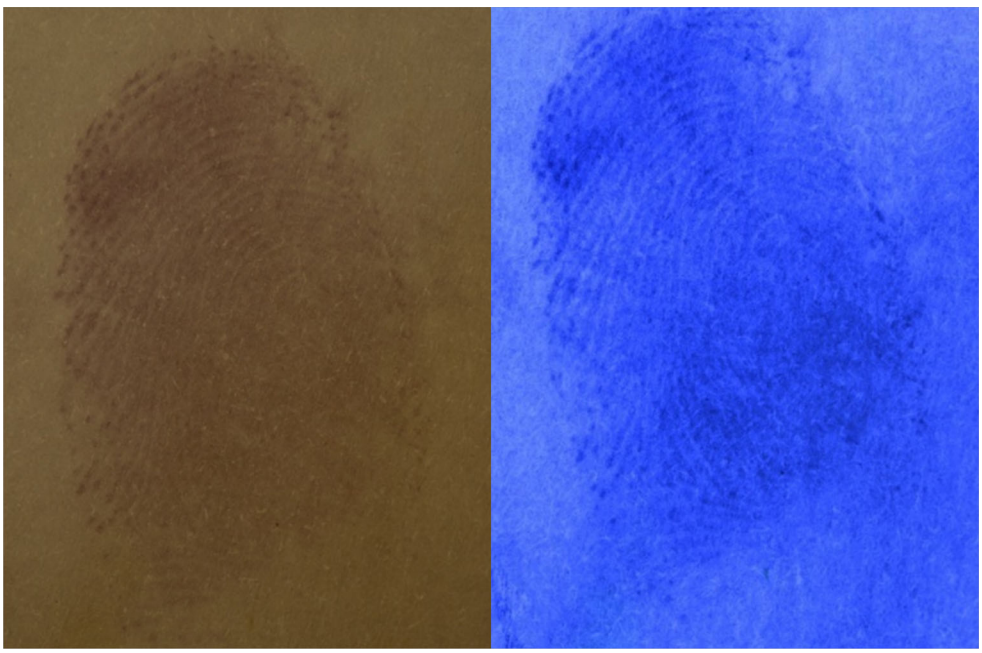


Fig. 7 Latent fingerprints developed on paper using **12a** (left: in daylight; right: at 365 nm)

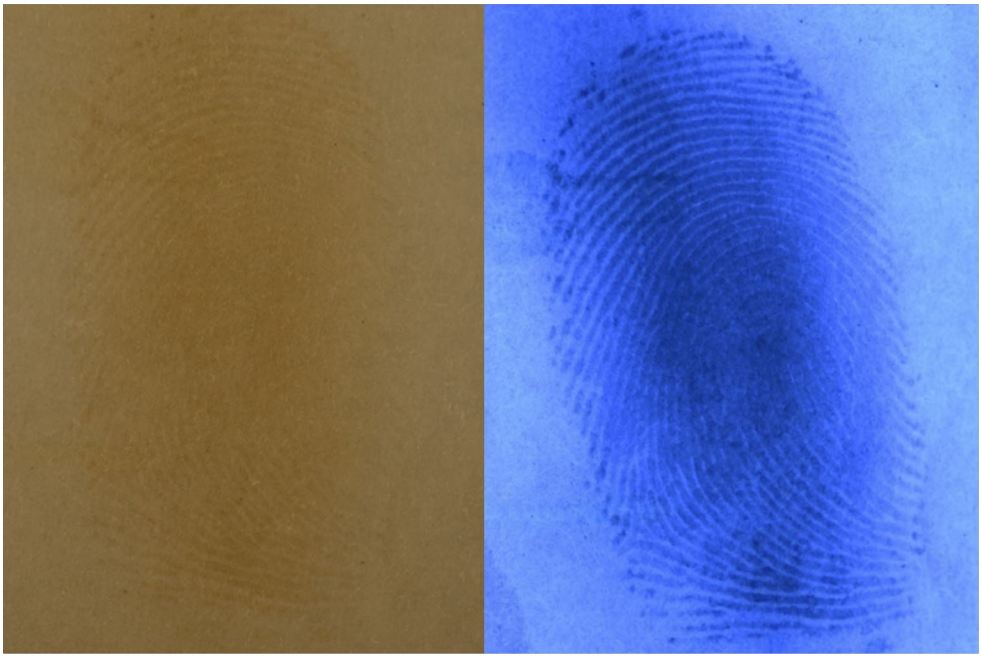


Fig. 8 Latent fingerprints developed on paper using **12b** (left: in daylight; right: at 365 nm)

Experimental

Chemicals and solvents were purchased from major chemical suppliers (Merck Millipore, Darmstadt, Germany; Acros Organics, Geel, Belgium; Sigma-Aldrich, St. Louis, MO, USA) with the highest purity grade. All solvents were dried by standard methods and distilled prior to use. Celite® 545 (Acros Organics), flux-calcined diatomaceous earth, was used as filter agent. Thin-layer chromatography was performed on Merck Millipore precoated aluminium TLC plates with silica gel 60 F_{254} (hexanes/EtOAc).

Melting points were measured on a Kofler hot stage. IR spectra were acquired on Nicolet FT-IR-ATR 6700 (Thermo Fisher Scientific, US) spectrometer and are given in cm^{-1}. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 300 MHz and 75 MHz, respectively, on a Varian VNMRS 300 MHz spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as internal standard. Chemical shift values were recorded in δ units (ppm) and coupling constants (J) expressed in Hertz (Hz). Elemental analyses (C, H, N, S) were conducted using a Carlo Erba Strumentazione 1106 apparatus (Carlo Erba Strumentazione, Milan, Italy), and their results were found to be in good agreement ($\pm$ 0.3%) with the calculated values.

4-Hydroxy-7-methoxy-2*H*-chromen-2-one (**9b**) [27] and 4-bromo-2*H*-chromen-2-one (**10a**) [28] were prepared according to the literature procedures. The structures of the prepared compounds were proven by ^{1}H NMR spectra and by measuring their melting points.

4-Bromo-7-methoxychromen-2-one (10b) A mixture of 400 mg chromen-2-one **9b** (2.08 mmol) and 775 mg $POBr_3$ (2.70 mmol) was stirred at 130 °C for 2 h and at 160 °C for an additional 15 min. The mixture was cooled to room temperature, and 100 g of ice was added to the resulting dark brown mixture. After allowing the mixture to stand overnight, a brown precipitate was collected, washed well with water, dried and recrystallised from EtOH to give 370 mg (70%) of **10b** as orange solid. M.p.: 88–90 °C (EtOH); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 3.88 (s, 3H, OMe), 6.89 (s, 1H, H-3), 7.03–7.06 (m, 2H, H-4, H-5), 7.72 (d, J = 8.4 Hz, 1H, H-8) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 56.68, 101.31, 112.47, 113.63, 116.21, 129.28, 141.25, 154.24, 158.78, 163.94 ppm. The IR spectrum was found to be identical to the one described in Ref. [29].

4-(1-Oxo-2,3-dihydro-1*H*-inden-5-yloxy)-2*H*-chromen-2-one (11a, $C_{18}H_{12}O_4$) A mixture of 300 mg 5-hydroxyindanone (**8**, 2.02 mmol) and 550 mg K_2CO_3 (4.04 mmol) in 60 cm^3 of dry acetonitrile was stirred for 30 min at room temperature. Bromocoumarin **10a** (460 mg, 2.02 mmol) was added in one portion and the reaction mixture was refluxed for 10 h. After cooling to room temperature, 70 g of ice was added to the mixture. The brown precipitate was collected, washed well with water, dried, and recrystallised from acetone to give 420 mg (71%) of **11a** as yellow solid. M.p.: 162–164 °C (acetone); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.79 (t, 2H, Ar–C$\underline{H_2}$–CH_2–CO), 3.21 (t, 2H, Ar–CH_2–C$\underline{H_2}$–CO), 5.48 (s, 1H, H-3), 7.21 (dd, J = 8.3 Hz, 2.0 Hz, 1H, H-6′), 7.31 (d, J = 2.0 Hz, 1H, H-4′), 7.34–7.43 (m,

2H, H-6, H-8), 7.65 (ddd, J = 8.6 Hz, 7.3 Hz, 1.5 Hz, 1H, H-7), 7.89 (d, J = 8.3 Hz, 1H, H-7′), 8.01 (dd, J = 7.9 Hz, 1.5 Hz, 1H, H-5) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.86, 36.44, 94.41, 115.11, 117.01, 119.27, 120.95, 122.99, 124.29, 126.16, 133.12, 135.56, 153.71, 157.57, 157.67, 162.15, 165.60, 204.91 ppm; IR (neat): $\bar{\nu}$ = 1703, 1621, 1605, 1262, 1231, 1180 cm^{-1}.

7-Methoxy-4-(1-oxo-2,3-dihydro-1*H*-inden-5-yloxy)-2*H*-chromen-2-one (11b, $C_{19}H_{14}O_5$) A mixture of 174 mg 5-hydroxyindanone (**8**, 1.17 mmol) and 325 mg K_2CO_3 (2.35 mmol) in 40 cm^3 of dry acetonitrile was stirred for 30 min at room temperature. Bromocoumarin **10b** (300 mg, 1.17 mmol) was added in one portion and the reaction mixture was refluxed for 10 h. After cooling to room temperature, 35 g of ice was added to the mixture. The brown precipitate was collected, washed well with water, dried and recrystallised from acetone to give 250 mg (67%) of **11b** as yellow solid. M.p.: 224–227 °C (acetone); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.78 (t, 2H, Ar–C$\underline{H_2}$–CH_2–CO), 3.19 (t, 2H, Ar–CH_2–C$\underline{H_2}$–CO), 3.91 (s, 3H, OCH_3), 5.33 (s, 1H, H-3), 6.87 (d, J = 2.3 Hz, 1H, H-8), 6.93 (dd, J = 9 Hz, 2.4 Hz, 1H, H-6′), 7.19 (dd, J = 8.4 Hz, 2.3 Hz, 1H, H-6), 7.29 (d, J = 2.4 Hz, 1H, H-4′), 7.85–7.90 (m, 2H, H5, H-7′) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.81, 36.41, 55.85, 91.75, 100.65, 108.28, 112.64, 119.23, 120.95, 124.05, 126.04, 135.40, 155.62, 157.59, 157.65, 162.69, 163.81, 165.92, 204.94 ppm; IR (neat): $\bar{\nu}$ = 1718, 1692, 1624, 1603, 1290, 1239, 1152 cm^{-1}.

2,2-Dihydroxy-5-(2-oxo-2*H*-chromen-4-yloxy)-2*H*-indene-1,3-dione (12a, $C_{18}H_{10}O_7$) A mixture of 220 mg freshly sublimed, pulverised SeO_2 (2.05 mmol), 1 cm^3 of water, and 20 cm^3 of dioxane was stirred at 60 °C until homogeneous (1 h). Indanone **11a** (150 mg, 0.51 mmol) was added in one portion, and the reaction mixture was refluxed for 2 h. The hot reaction mixture was filtered through Celite® and washed with 30 cm^3 of dioxane. The filtrate was discoloured with activated charcoal, filtered through a pad of Celite®, and the solvent was removed under reduced pressure. The crude product was recrystallised from water to give 110 mg (63%) of **12a** as white solid. M.p.: 123–126 °C (H_2O); ^{1}H NMR (300 MHz, DMSO-d_6): δ = 5.67 (s, 1H, H-3), 7.44–7.53 (m, 2H, H6, H-8), 7.64 (s, 2H, OH), 7.74–7.80 (m, 1H, H-7), 8.00–8.04 (m, 3H, H-5, H-4′, H-6′), 8.18 (dd, J = 8.1 Hz, 0.9 Hz, 1H, H-7′) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 88.31, 96.17, 115.18, 116.40, 117.07, 123.55, 125.02, 127.41, 130.53, 133.94, 136.75, 141.56, 153.61, 159.66, 161.43, 164.95, 196.16, 196.63 ppm; IR (neat): $\bar{\nu}$ = 3260, 1759, 1720, 1677, 1623, 1593, 1257, 1230, 1194 cm^{-1}.

2,2-Dihydroxy-5-(7-methoxy-2-oxo-2*H*-chromen-4-yloxy)-2*H*-indene-1,3-dione (12b, $C_{19}H_{12}O_8$) A mixture of 137 mg freshly sublimed, pulverised SeO_2 (1.24 mmol), 0.6 cm^3 of water, and 12 cm^3 of dioxane was stirred at 60 °C until homogeneous (1 h). Indanone **11b** (100 mg, 0.31 mmol) was added to one portion, and the reaction mixture was refluxed for 2 h. The hot reaction mixture was filtered through Celite® and washed with 20 cm^3 of dioxane. The filtrate was discoloured with activated charcoal, filtered through a pad of Celite®, and the solvent was removed under reduced pressure. The crude product was recrystallised from water to give 69.5 mg (61%) of **12b** as brown-yellow solid. M.p.: 159–161 °C (H_2O); ^{1}H NMR (300 MHz, DMSO-d_6): δ =3.90 (s, 3H, OCH_3), 5.48 (s, 1H, H-3), 7.04 (dd, J = 8.7 Hz, 2.1 Hz, 1H, H-6′), 7.11 (d, J = 2.1 Hz, 1H, H-4′), 7.61 (s, 2H, OH), 7.90 (d, J = 9 Hz, 1H, H-5), 7.96–8.01 (m, 2H, H-6, H-8), 8.16 (d, J = 8.7 Hz, 1H, H-7′) ppm; ^{13}C NMR (75 MHz, DMSO-d_6): δ = 56.10, 87.86, 92.89, 100.82, 107.79, 112.54, 115.83, 124.26, 126.86, 130.01, 136.21, 141.06, 155.17, 159.23, 161.36, 163.52, 164.82, 195.66, 196.15 ppm; IR (neat): $\bar{\nu}$ = 3233, 1765, 1721, 1682, 1621, 1594, 1233, 1161 cm^{-1}.

Spectral study and development of fingerprints

Fluorescence spectra were measured in a 1 cm cuvette with an FSP 920 (Edinburgh Instruments, UK) spectrofluorimeter in front-face arrangement to avoid the self-absorption effect. Fingerprint images were taken by DSC4 Fingerprint Imaging System (Foster + Freeman, UK) with Crime–lite® 8 × 4, 365 nm filter.

Working solution: 10 mg of ninhydrin derivative **12** was dissolved in 0.13 cm^3 EtOH, followed by the addition of a drop of ethyl acetate and a drop of glacial acetic acid. The prepared solution was diluted with 0.10 cm^3 of HFE-7100 (methoxynonafluorobutane, Sigma-Aldrich).

Fingerprints: Latent fingerprints were collected on a white paper (standard copy paper, 80 g/m^2) from donors who had not consumed food or handled chemicals 30 min prior to providing specimen fingerprints. Donors were instructed to gently place fingertips onto the paper and not to remove their hands until fingers had been outlined in graphite pencil. The paper substrate was left to age for 2 days in a dark place and then immersed into the prepared working solution. The paper was air dried at room temperature and heated in an oven at 150 °C.

Acknowledgements This publication is the result of the project implementation: Centre of Excellence in Security Research supported by the Research and Development Operational Programme funded by the ERDF. Grant Number: ITMS 26240120034.

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