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Developing fingermarks on porous surfaces with the use of genipin in the gaseous phase

Summary

The article presents the results of studies on the method of sensibilizing dactyloscopic traces directly from the gaseous phase. The detection of dactyloscopic traces on absorbtive surfaces requires specific revealing methods, whose essential aspect is the need to deliver reagent to the place of occurrence of the corresponding component of trace forming substance. In practice, for many years, various types of solutions have been used for this purpose, such as DFO, ninhydrin and 1,2-indanedione. Within the framework of this study, research was carried out on revealing fingerprints on absorptive surfaces with the use of genipin, under reduced pressure conditions and in order to compare against the liquid phase. Based on the results of the tests carried out and results obtained, it should be stated that the genipin vacuum sublimation technique can be successfully used to reveal fingerprints on absorptive surfaces. The traces revealed are visible both under white light and fluorescence illumination. The effectiveness of the dactyloscopic trace sensibilization method in the gaseous phase has been demonstrated with regard to such substances as ninhydrin and genipin.

Keywords genipin, amino acids, absorbtive surfaces, sublimation, dactyloscopic trace

1. Introduction

Revealing dactyloscopic traces on absorptive surfaces requires the use of specific methods. In everyday laboratory practice, mainly chemical methods are used, directed at amino acid components of trace forming substance, such as DFO, ninhydrin and 1,2-indanedione [1,2]. In the case of fatty components of trace forming substance, powder-based methods or Physical Developer are applied.

An essential part of the process of revealing dactyloscopic traces on absorptive surfaces is to deliver reagent to the place of occurrence of the corresponding component of trace forming substance. In practice, for many years, various types of solutions have been used for this purpose. When selecting the components of a solution, the following factors are taken into account:

- revealing reagent's solubility, stability of the solution,
- minimal negative impact on the surface and trace forming substance, avoiding a blur effect on inks,
- rate of evaporation,
- the ability to quickly penetrate the fibrous structure of paper,
- low flammability,
- low impact on health and the environment.

In order to obtain the best recipes, a number of chemical compounds are being tested, such as HFE7100, HFE71DE, methanol, ethyl acetate and acetic acid, used both as solvents and additives. In many

cases, liquid components of the solution can cause both the dissolution of the trace forming substance and a blur effect on the trace deposited. Without a doubt, they can also lead to the destruction or loss of biological material. Significant progress achieved over the years in creating new revealing recipes, caused a withdrawal from the use of environmentally harmful freon or flammable ethers and acetone, which were replaced with fluoroethers. Still, the use of liquid-based methods can result to a certain extent in a negative impact on traces or the surface.

Meanwhile, an interesting option is the possibility of deposition of sensibilizer vapours from the gaseous phase directly onto the trace forming substance, disregarding the solvents. Effective process handling requires the conditions of reduced pressure and heating the revealing substance below the threshold of its thermal decomposition. The ideal sensibilizers are the substances that selectively react with amino acids, while simultaneously forming an optically active compound. The substances exhibiting such properties include: DFO, 1.2-indanedione, ninhydrin, or genipin. Within the framework of this study, research was carried out on revealing fingerprints on absorptive surfaces with the use of genipin, under reduced pressure conditions and in order to compare in the liquid phase. In addition, the method of sensibilizing traces with genipin in the gaseous phase was compared against the standard ninhydrin method.

2. Theoretical background

In the early 60s of the last century, Djerassy et al. discovered the structure of a natural chemical compound with the molecular formula $C_{11}H_{14}O_5$, which received the name genipin. This colorless compound easily generated a blue-purple hue upon contact with the skin. A similar reaction was observed with amino acids. Genipin is produced from natural ingredients, namely gardenia (*Gardenia jasminoides*) fruit extract, by hydrolysis of iridoid glycoside called geniposide [3].

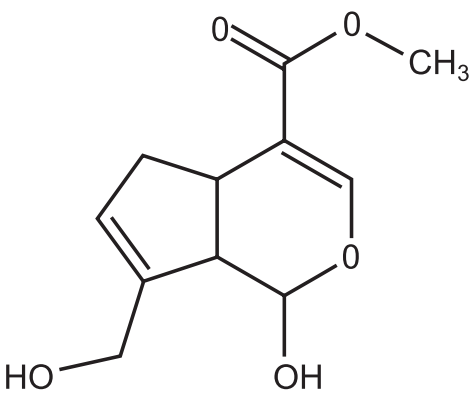

Fig. 1. Structural formula of genipin.

The first reports on the application of genipin in dactyloscopy date back to the beginning of the 20th century. At that time, the fluorescent properties of the genipin-amino acids reaction products were demonstrated. The study involved the selection of the optimal recipe, solvent, pH, conditions for revealing and fluorescent properties with different amino acids. As a result, the possible benefits stemming from the implementation of genipin into practice were pointed out, namely:

- dual effect – colorful and fluorescent product obtained in one reaction without the need for a DFO – ninhydrin sequence (excitation wavelength: 590 nm, maximum emission wavelength: 630 nm),
- fluorescence shifted towards longer wavelengths as compared with DFO. As a result, higher signal-to-noise ratio is obtained, due to the fact that many paper surfaces exhibit fluorescence within the range of 500–600 nm, or documents with inks exhibiting fluorescence within the same range,
- safety related to the use of genipin in the laboratory [4].

Studies have shown that genipin is almost as sensitive as ninhydrin and DFO in terms of generating a colorful or fluorescent reaction product, respectively. However, it was indicated that shifting the fluorescence towards longer wavelengths can be perceived as an advantage, particularly with regard to certain types of papers, which exhibit/support the fluorescence of surface or inks. Additionally, it was also shown that the genipin reaction mechanism is not identical for all amino acids present in the trace forming substance [2].

Revealing dactyloscopic traces by using sublimation under vacuum has been so far proposed only for ninhydrin. Fingerprints have been successfully revealed on regular and thermosensitive paper, as well as on euro banknotes. Optimal conditions included the vacuum in the range of 2 to 5 mbar, sublimation of 50 mg ninhydrin – 150°C for 30 minutes. The surfaces treated with ninhydrin were heated at 50°C and 50% relative humidity for 30 minutes in the air-conditioned chamber [5].

3. Equipment

The tests were carried out in a vacuum chamber dedicated to the cyanoacrylate method, with specially designed evaporator for carrying out the controlled sublimation. Attached to the polymethylmethacrylate chamber closing were four current ducts. Two of the ducts were used to power the heater, whereas the remaining two served for temperature measurements. The temperature was measured using a PT 100 probe, whose resistance was determined using a DIGITAL MULTIMETER RD701 form SANWA (Japan). The

construction of the chamber frame along with the closing is presented in figure 2.

Fig. 2. Chamber utilized in the studies, dedicated to the cyanoacrylate method, adapted for sublimation of other substances.

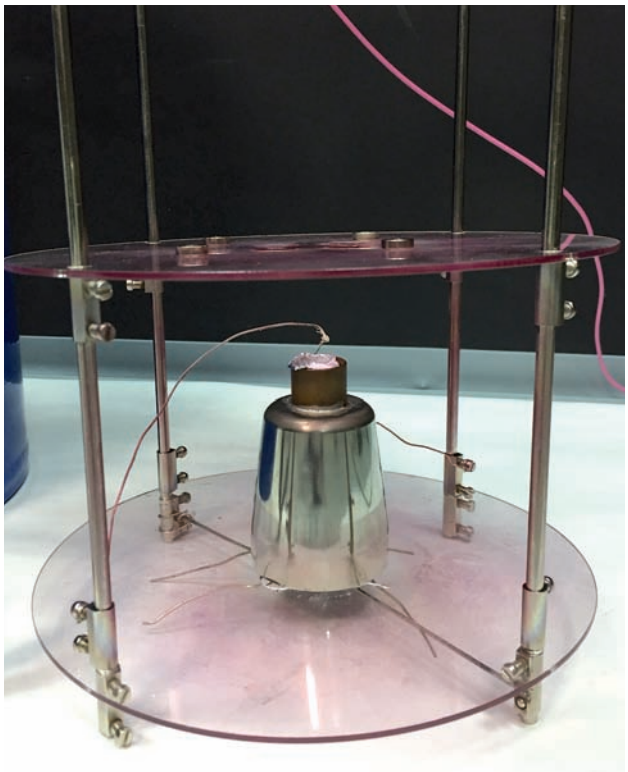

Fig. 3. Evaporator.

Figure 2 features the following components: a heater with thermal screen and PT 100 probe tips, a plate serving as the basis for the heater and constituting the bottom ring binding metal rods, which, at the same time, constitute the heater's power cables, connecting the probe with the meter. In addition, the item plate is visible, to which the test samples and test strips (SEMA) are mounted by means of magnets. It should be noted that the distance between the evaporator and the item plate is adjustable. The design of the test bench rack allows positioning of samples at different distances from the vapour source.

The evaporator is made of copper rod with a cavity in the upper part with a depth of 5 mm and a diameter of 15 mm. Inside the cavity, there is a separator made of aluminum foil, in which the weighed sample portion is placed.

4. Materials and methods

4.1. Chemical reagents

Ninhydrin (2.2-dihydroxy-1.3-indanedione) was purchased from BVDA (the Netherlands), while Genipin from CBC Challenge Bio products CO. LTD. (Taiwan). Anhydrous ethanol and acetic acid 99.8% were received from Honeywell (Germany), ethyl acetate from CHEMPUR (Poland), HFE 7100 from SIRCHIE (U.S.), and ethanol from POCH (Poland).

All chemical reagents used in this study were of analytical grade, used without subsequent purification.

4.2. Preparation of solutions

4.2.1 Genipin solution

0.425 g of genipin was dissolved in a mixture consisting of 14.25 ml anhydrous ethanol and 21.5 ml ethyl acetate. These ingredients were then stirred on a magnetic stirrer until genipin crystals were completely dissolved. Finally, the solution was spiked with 146.75 ml HFE7100 and stirred for 10 minutes.

4.2.2 Ninhydrin solution

As a first step, a concentrated solution was prepared by weighing out 12.5 g of ninhydrin, and then adding 12.5 ml of acetic acid 99.8%, 112.5 ml of ethanol 99.8% and 5 ml of ethyl acetate. The solution was stirred on a magnetic stirrer until ninhydrin was completely dissolved. The second step involved preparation of a working solution by combining 26 ml of ninhydrin concentrate with 500 ml of HFE 7100 and stirring the solution on a magnetic stirrer for 10 minutes.

4.3 Preparation of test samples

Absorptive surfaces in the form of plain paper (80 g/m^2) were subjected to analysis. The sheets of paper were cut into strips. 10 strips of paper and 15 amino acid test strips SEMA (Germany) were used in the experiments. Fingerprints on paper strips were deposited by a single person, using the index finger, which had been previously rubbed against the cheek. The samples in the form of amino acid test strips were immersed for

5 seconds in Petri dishes containing the appropriate solution and then dried at room temperature.

The prepared trace samples were divided into two groups, 5 pieces in each. Each of the samples was additionally cut in half. Next, both groups were exposed to genipin in the liquid and gaseous phase, and ninhydrin in the liquid phase. All the samples used in the study were kept under constant temperature and humidity conditions.

4.4 Sensibilization in the gaseous phase

The samples in the form of paper strips carrying the traces were placed on the item plate of the vacuum chamber rack, next to the amino acids test strips. After closing the apparatus, the vacuum was generated and the process of evaporation or sublimation of the corresponding sensibilizer was initiated. The trials conducted have indicated that the sample-to-evaporator distance of approximately 6 cm was the most appropriate for the vacuum (pressure) achieved inside the chamber.

The vacuum was generated using a rotary pump, and the final pressure was not lower than 10^{-2} mm Hg (about 1 Pascal). The temperature of the evaporator (during sublimation or evaporation) was controlled and adjusted in the range of 120–150°C. The average duration of the trace revealing process, involving pumping the tank until the lowest pressure was obtained, heating the evaporator to the required temperature and the transition from the solid to the gaseous phase was no more than 10 min.

After the sensibilization stage, the vacuum chamber was aerated in a controlled manner and the samples prepared in this way were transferred to the Weiss-Gallenkamp climatic chamber. The sensibilizer-trace reaction proceeded for about 1 hour at a temperature of 80°C and a relative humidity of 80%. Observation, registration and analysis of the results were performed using a macroscopic hyperspectral imaging system based on liquid crystal tunable filter (LCTF) technology – VIS CONDOR Macroscopic Chemical Imaging SystemTM (ChemImage, U.S.).

After sublimation/evaporation and aeration of the apparatus, the samples were placed in the Weiss-Gallenkamp climatic chamber for ensuring optimal fingerprint revealing conditions, i.e. a temperature of approximately 80°C and a relative humidity of approximately 65%. The samples were heated for 1 hour.

4.5 Registration of hyperspectral images of the revealed fingerprints

The intensity of fluorescence emitted or the absorption of samples were measured by using a macroscopic hyperspectral imaging system – CONDOR Macroscopic Chemical Imaging SystemTM (ChemImage, U.S.). The reacted sample surfaces were scanned (within the areas occupied by traces and reactive areas of the test strips) and analyzed using ChemXpert software. The fluorescence measurements were taken at 600–720 nm and the spectral resolution of 7 nm. The fluorescence was induced at 575 nm with a Mini Crime Scope forensic illuminator (Ybon, U.S.). Absorption measurements were performed in the range of 470–720 nm. In order to measure the absorption, the measurement data were transformed using the $-\mathrm{Log}T/T_0$ function.

Averaged results of four series of experiments (2 series of 10 test strips, and 2 sets of 5 traces divided into two parts) were subjected to analysis. In the case of SEMA test strips, four reaction fields of exponentially declining amino acid levels were analyzed, while in the case of paper strips with deposited fingerprints, the areas exhibiting the colorful reaction products were selected. Numerical data from the measurements were transferred to a Microsoft Excel spreadsheet.

5. Results

Genipin vacuum sublimation technique can be successfully used to reveal fingerprints on absorptive surfaces. The traces revealed are visible under both white light and fluorescence conditions – figures 4, 5. The traces revealed using this technique do not show blurring or disappearance of papillary line patterns. In addition, the poroscopic features of the ridges were well exposed. It should be assumed that this was due to the absence of capillary phenomena responsible for distortions of papillary line patterns, characteristic for absorptive surfaces. Moreover, any destructive influences by phenomena associated with the occurrence of surface tension on the drops formed were avoided.

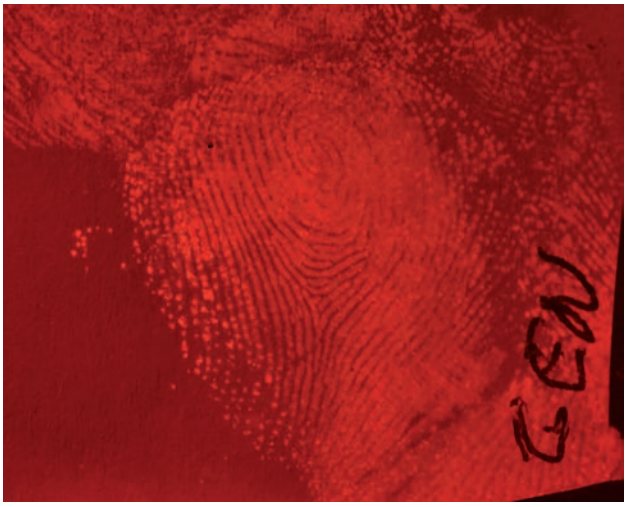

Fig. 4. Fingerprints revealed using genipin vacuum sublimation technique – a view in the fluorescence mode (excitation 575 nm, red longwave edge filter).

Fig. 5. A fingerprint revealed using genipin vacuum sublimation technique – a view under white light.

The measurement data obtained from the test strips indicated that the level of fluorescence emitted by traces revealed with genipin vacuum sublimation technique was comparable to that observed for traces revealed by means of liquid techniques – figures 6, 7. The same was true in the case of test fingerprints. It should be noted, however, that the precision of defining the measurement area as well as the prevalence of amino acids were much higher on the test strips as compared with the test traces. Plausibly, the above was the reason for recording the discrepancy of measurement data related to the test trace no. 3 – figures 8, 9.

The conducted experiments indicated that the optimum genipin evaporation temperature is 140°C. It is very important to control the rate of increase of the evaporator temperature, as exceeding the optimal range may result in thermal decomposition of genipin. In addition, the samples after trace revealing required heating at 80°C and a relative humidity of 80%, in contrast to ninhydrin, which requires a relative humidity of 62%.

The measurement data related to the absorption of vacuum sublimed genipin are comparable with those obtained for ninhydrin solution. However, certain spectral differences are apparent and translatable

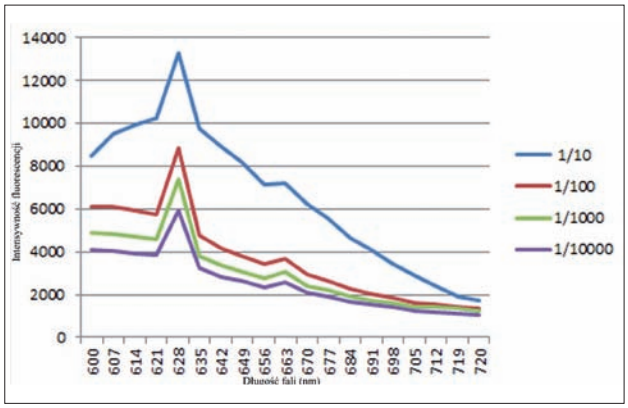

Fig. 6. Fluorescence of four SEMA test strip reaction fields with exponentially decreasing order of amino acid concentration, treated with genipin vacuum sublimation technique.

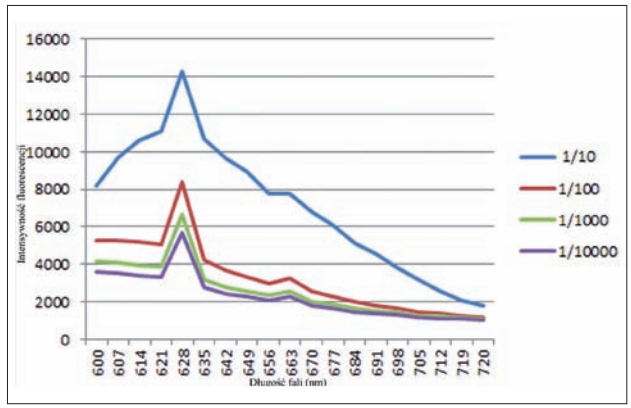

Fig. 7. Fluorescence of four SEMA test strip reaction fields with exponentially decreasing order of amino acid concentration, treated with genipin solution.

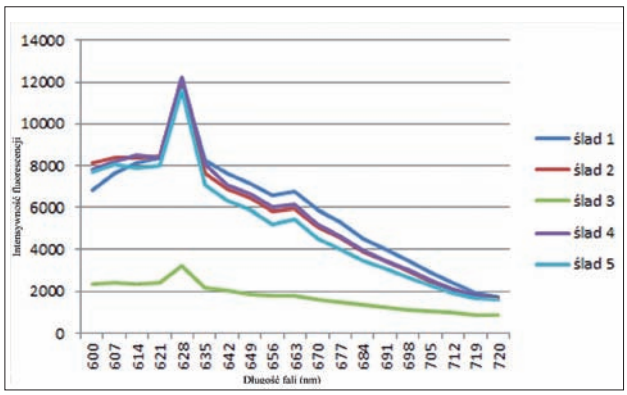

Fig. 8. Fluorescence of fingerprints treated with genipin vacuum sublimation technique.

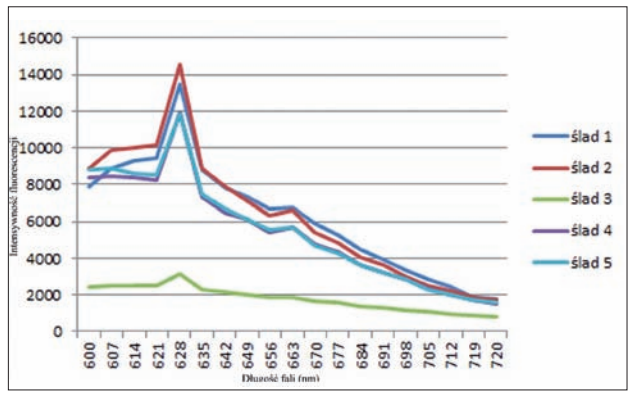

Fig. 9. Fluorescence of fingerprints treated with genipin solution.

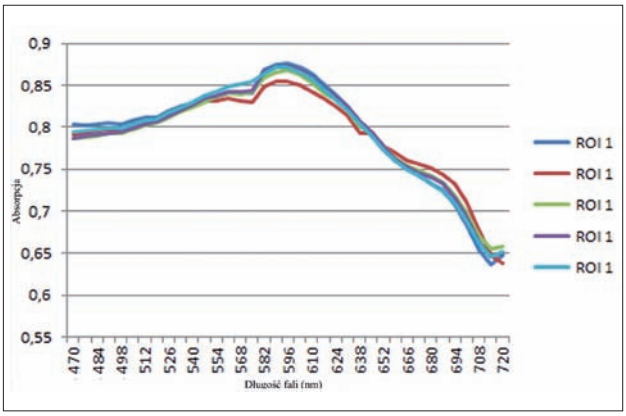

Fig. 10. Absorption of the SEMA test strip reaction field with the highest amino acid concentration, treated with genipin vacuum sublimation technique.

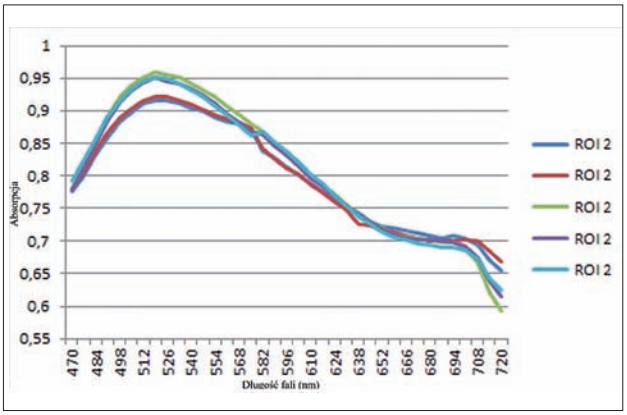

Fig. 11. Absorption of the SEMA test strip reaction field with the highest amino acid concentration, treated with ninhydrin solution.

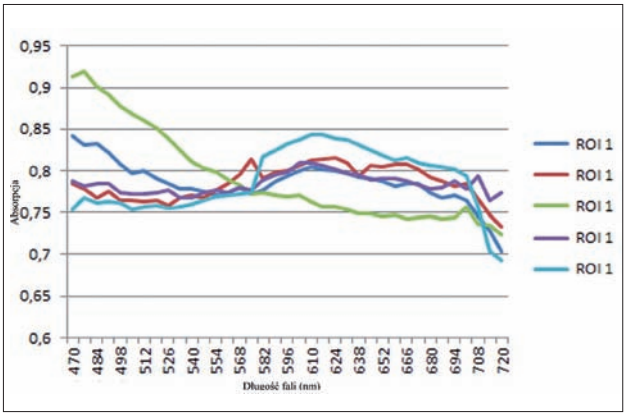

Fig. 12. Absorption of fingerprints treated with genipin vacuum sublimation technique.

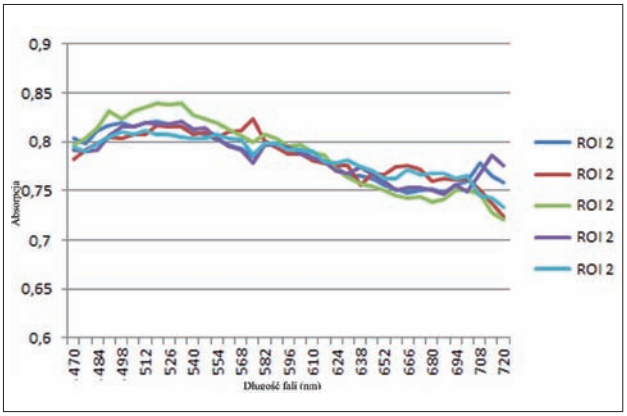

Fig. 13. Absorption of fingerprints treated with ninhydrin solution.

into different colors of the reaction products of both substances with amino acids – figures 10–13.

6. Conclusions

The method of sensibilizing dactyloscopic traces directly from the gaseous phase has the potential of becoming a very important tool, complementing the currently available arsenal of revealing techniques. This method is very simple and requiring relatively inexpensive equipment. The sensibilization process is short and, in addition, it does not cause degradation or loss of material suitable for genetic research. It should be pointed out that the effectiveness of the dactyloscopic trace sensibilization method in the gaseous phase has been demonstrated with regard to such substances as ninhydrin and genipin. Consequently, it can be anticipated that further research will confirm the usefulness of other substances in this approach.

Sources of figures:

Figure 1: Almog J., Cohen Y., Azoury M., Hahn T.R., Genipin – A Novel Fingerprint Reagent with Colorimetric and Fluorogenic Activity, J. Forensic Sci., 2004, no. 49, p. 2

Figures 2–13: authors

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Translation Rafał Wierzchosławski