The identification of the components, molecular structures and quality of stamp ink from gambier extract

S Silfia*, S Sofyan, F Failisnur dan G Yeni
Institution of Research and Standardization of Industry - Padang
Jl. Raya LIK No. 23 Ulu Gadut, Padang, Indonesia
Email: silfiabintiarsul@gmail.com

Abstract. Stamp ink is a major product of gambier plant (Uncaria gambir) extracts. Its level of tannins is usually high, making it an ideal raw material in the production of dyes and stamp ink. Hence, it is necessary to identify these color forming components in stamp ink. The aim of this study was to identify the components, molecular structures, and the quality of gambier stamp ink complexed with FeSO₄. Five samples of the ink were complexed with 30%, 25%, 20%, 15% and 10% FeSO₄. The Gas Chromatography - Mass Spectrometry (GC-MS) showed the optimum results with 25% FeSO₄ treatment. It contained 11.44% pyrocatechol, 3.74% glycerol, and 2 Propanol, 1 Amina 81.98%, with clearer printings on paper compared with other treatments.

1. Introduction
Gambier extract contains about 20 - 55% of tannin, 7 -33% of catechins and 20 -30% of pyrocatechol [1,2]. These three compounds are natural phenols with flavonoid structures [3–6]. It is a multifunctional plant used as dyes in textile industries [7,8], vegetable tanners [9–12], raw materials in pharmaceutical and cosmetic products [13], and inks [6,14,15].

Ink is a colored liquid, used for personal needs, office administration, organization, and institution. The stamp, usually used with ink, represents the identity of an institution. In addition, some of its components are toxic in nature, which could have a negative impact on one’s health [4,6,15,16]. However, gambier extract was used as the raw material in this study due to its high tannin content, environmentally friendly, and readily available, with a production of about 14,220 tons in 2016 [17].

There are various studies on the use of tannins for ink production from other natural ingredients such as lemongrass oil, coffee grounds, resident fruit, flaxseed oil, and soybean seeds [18–21]. However, only gambier’s tannin complexed with FeCl₃ forms a blackish-blue color, red color with NaOH, and brownish color with Al₂(SO₄)₃ [15,22,23]. Additionally, ink with NaOH and Al₂(SO₄)₃ produces compounds with OH and CO groups from phenol and alcohol respectively. Furthermore, homogeneous particle size distribution usually comes up with a clear printing on papers [15].

The use of FeCl₃ as a complexing agent gives blackish-blue color with high intensity, which is also hazardous to health [16]. Hence, FeSO₄ was used as the complexing compound in this study due to its safe nature [24]. FeSO₄ was also used as a mordant in the coloring of textile with gambir [25–30].

2. Experimental

2.1 Materials and tools
The research was conducted at the laboratories of the Research Institute and Industrial Standardization in Padang, and the Post Harvest Center in Bogor. The materials used include; raw gambier (Uncaria gambier Roxb) from South Pesisir Regency farmers, technical ethanol 70%, glycerin, and FeSO₄ produced by Bratachem. The equipments used were; glassware, 100 mesh filters, seals, stamp pads, Gas Chromatography-Mass Spectrometry (GC-MS).

2.2 Research implementation
There were two steps involved in making stamp ink, these were the re-extraction of gambier, and the addition of FeSO₄ as complexing compounds. The first step re-extraction of gambier this process was carried out by smoothing gambier, then dissolved in hot water at about 90-100°C with a ratio of 1: 4. This was subjected to heating at 60°C for 5 hours and filtered to remove the impurities. The solution was decanted for 12 hours, its sediment was taken, the precipitate was dried at room temperature, and then sieved with a 100 mesh sieve. Then, the gambier granules were dissolved in technical ethanol 70% at a ratio of 1: 4 and stirred at a speed of 250 rpm at 60°C for 5 hours. Furthermore, it was allowed to stay for 24 hours, then filtered and both the filtrate and sediment were removed according to the recommended method [15].

In the second step, stamp ink formulations were added to FeSO₄ as complexing compounds. The formula used in making the stamp ink determines its level of compactness when printed on papers. The study was conducted with various percentages of FeSO₄ complexing compounds, such as 30%, 25%, 20%, 15%, and 10%. Also, 15% H₂O, 15% glycerin, and 10% violet crystals was added to each treatment and the solution stirred continuously at 250 rpm for 5 hours at 60°C until it was homogeneous in nature.

2.3 Observation
The stamp ink was subjected to analysis to determine its components and molecular structures using Gas Chromatography-Mass Spectrometry (GC-MS) QP2010S Shimadzu, and Agilent HP 1 column of 30 meters long with helium carrier gas used with a pressure of 13.7 kPa. In addition, the helium flow rate was 20 mL / min, and the column temperature ranged from 70°C to 310°C [30].

3. Results and discussion

3.1 Chromatogram as the main component of stamp ink
The constituent components of stamp ink with the use of 30% FeSO₄ were expressed and identified in GC-MS, as shown in figure 1a. The chromatograms showed the presence of five compounds which include; Pyrocatechol, 1,3 benzenediol, 4 Methyl Catechol, Glyceraldehyde and N-(Methyl-D2) -Aniline. However, the three dominant components are pyrocatechol (42,50%), 4 methyl catechol (16,17%) and glyceraldehyd (32,13%), with pyrocatechol as the largest (table 1). Identification of each compound in the chromatogram was carried out by matching the MS spectrum of each peak with Wiley’s database as shown in figures 1b and 1c. Then, figure 1b shows the peak spectrum of pyrocatechol with a treatment of 30% FeSO₄, while figure 1c is the pyrocatechol reference spectrum for Wiley’s database.

The chromatogram with 25% FeSO₄ treatment showed the presence of four compounds, which were; pyrocatechol (11,44%), glycerol(3,75%) dan 2 Propanol, 1 Amino(81,98%) (table 1) and a chromatogram with an unknown name, as shown in figure 2a. Also, the highest chromatogram was 2 Propanol, 1 Amino, matched with the reference spectrum according to the Wiley's database at 13,517 minutes as shown in figures 2b and 2c.
**Figure 1a.** Stamp ink chromatogram with 30% FeSO₄.

**Figure 1b.** Pyrocatechol peak spectrum according to Wiley's database of stamp ink spectra with 30% FeSO₄.

**Figure 1c.** Pyrocatechol reference spectrum according to Wiley's database of stamp ink spectra with 30% FeSO₄.

**Figure 2a.** Stamp ink chromatogram with 25% FeSO₄.
Figure 2b. Peak 2-Propanol,1-amino spectrum according to Wiley's database of stamp ink spectra with 25% FeSO₄.

Figure 2c. The 2-Propanol,1-amino reference spectrum according to Wiley's data base of stamp ink spectra with 25% FeSO₄.

The peak of the chromatogram with 20% FeSO₄ treatment showed the presence of four compounds; pyrocatechol, glycerol, methyl catechol and methyl ester. However, the three dominant ones as shown in figure 3a are pyrocatechol (60.76%), glycerol (31.74%), and methyl catechol (6.86%) (table 1). Also, the peaks from the molecular structure analysis are shown in figures 3b and 3c. In addition, the dominant peak was pyrocatechol, matched with the reference spectrum according to Wiley's data base at a retention time of 12,620 minutes.

There were fifteen compounds in the chromatogram with 15% FeSO₄, which included; silanediamine, phenol, glycerol, pyrocatechol, quinoline, N-methylindole, 3-methylquinoline, 3-methylindole, 1,3-dienyl-benzene, palmitic acid, octadecanoate, benzenamine, 4-hydroxycyclohexanone (appeared twice with different retention times), and one unknown chromatogram (figure 4a). However, the three dominant ones were phenol(3.32%), glycerol(80.73%), and pyrocatechol (4.20%) (table 1), with glycerol the highest, as shown in figure 4b. This was matched with the reference spectrum according to Wiley's database at a retention time of 11,243 minutes, as shown in figure 4c.

Figure 3a. Stamp ink chromatogram with 20% FeSO₄.
Figure 3b. Pyrocatechol Peak Spectrum according to Wiley's data base of stamp ink spectra with 20% FeSO₄.

Figure 3c. Pyrocatechol reference spectrum according to Wiley's data base of stamp ink spectra with 20% FeSO₄.

The components that appeared in the stamp ink with the FeSO₄ complexed were pyrocatechol, 4 methyl catechol, 1,3 benzendiol, phenol (phenolic compounds) and glicerol, gliceraldehyde 2-propanol, 1-amine classified as alcohol compounds [30]. The function of phenolic compounds as reductants/free radical scavengers, in plant physiology played a role in the formation of color/pigmentation, causing tastes such as sweet and bitter, for growth, reproduction and for plant resistance to pathogens and predators [25,27,28]. Glycerol, gliceraldehyde (alcohol which forms a structure with an O-H group and 2 propanol, 1 amino and bound to an amine group) [26,31].

Figure 4a. Stamp ink chromatogram with 15% FeSO₄.
Figure 4b. The glycerol peak spectrum according to Wiley's database of stamp ink spectra with 15% FeSO₄.

Figure 4c. The glycerol reference spectrum according to Wiley's database of stamp ink spectra with 15% FeSO₄

There were five compounds in the chromatograms with 10% FeSO₄ treatment, namely: glycerol, pyrocatechol, phenethyl alcohol, palmitic acid and methyl ester, as shown in figure 5a. However, the two dominant ones were pyrocatechol(1,63%) and glycerol(96,87%) (table 1). In terms of its molecular structure, glycerol had three hydroxyl (O-H) groups which easily absorbed water from the air [29]. The dominant peak was glycerol, matched with the reference spectrum according to Wiley's database at a retention time of 11,243 minutes. These are shown in figure 5b and 5c.

Figure 5a. Stamp ink chromatogram with 10% FeSO₄

Figure 5b. The glycerol peak spectrum according to Wiley's database of stamp ink spectra with 10% FeSO₄
The compound identified at a retention time of about 12 minutes was pyrocatechol, also the highest compound detected in the 30% FeSO₄ treatment with a percentage of 42.50%. This was followed by 60.76% in the 20% FeSO₄ treatment, 11.44% in the 25% FeSO₄ sample, 4.20% in 15% FeSO₄ and 1.63% in the 10% FeSO₄ treatment.

Also, the peak which appeared at a retention time of about 11 minutes was glycerol. However, its highest composition of 96.87% was found in the 10% FeSO₄ treatment. This was followed by 80.73% in the 15% FeSO₄, 31.74% in the 20% FeSO₄ and 3.75% in the 25% FeSO₄ treatment. In terms of its molecular structure, glycerol had three hydroxyl (O-H) groups which easily absorbed water from the air [29].

The methyl catechol appeared at a retention time of about 13 minutes, which was dominantly found in the 25% FeSO₄ treatment at 81.98%, and then followed by 16.17% in the 30% FeSO₄ and then 6.86% in the 20% FeSO₄. Also, phenol was detected at a retention time of about 9 minutes with 3.23% in the 15% FeSO₄ treatment.

Usually, phenols are important compounds in plant physiology due to its role in pigmentation, taste, growth, reproduction, as well as plants’ ability to resistance to pathogens and predators [25].

The dominant molecular structure of stamp ink appearing with the FeSO₄ complexed is shown in table 2, namely pyrocatechol, phenol, methyl catechol (classified as a flavonoid compound/O-H group). The O-H groups of phenolic compounds were reacted with metal compounds to form complexes that caused color in the ink [16,26,31]. Furthermore, there were 2-Propanol-1amine.

Table 1. The analysis results on the molecular structure of stamp ink with the use of FeSO₄.

| No. | FeSO₄ Concentration (%) | RT (min) | Compound Name            | Molecular Formula | Concentration (%) |
|-----|------------------------|----------|--------------------------|-------------------|------------------|
| 1   | 30%                    | 12.564   | Pyrocatechol             | C₆H₆O₂            | 42.50            |
|     |                        | 13.480   | 4 methyl catechol        | C₆H₆O₂            | 16.17            |
|     |                        | 13.933   | Gliceraldehid            | C₃H₆O₃            | 32.13            |
| 2   | 25%                    | 12.630   | Pyrocatechol             | C₆H₆O₂            | 11.44            |
|     |                        | 13.517   | 2 Propanol, 1-Amine      | C₄H₉NO            | 81.98            |
|     |                        | 12.620   | Glycerol                 | C₆H₁₀O₃           | 81.98            |
| 3.  | 20%                    | 12.620   | Pyrocatechol             | C₆H₆O₂            | 60.76            |
|     |                        | 12.817   | Glycerol                 | C₄H₁₀O₄           | 31.74            |
|     |                        | 13.520   | 4 Methyl catechol        | C₇H₈O₂            | 6.86             |
| 4   | 15%                    | 9.892    | Phenol                   | C₆H₆O             | 3.32             |
|     |                        | 11.105   | Gliceral                | C₄H₁₀O₄           | 80.73            |
|     |                        | 12.693   | Pyrocathechol            | C₆H₁₀O₂           | 4.20             |
| 5   | 10%                    | 11.243   | Glycerol                 | C₄H₁₀O₄           | 96.87            |
|     |                        | 12.744   | Pyrocathechol            | C₆H₆O₂            | 1.63             |
compounds, gliceraldehyd and glycerol which are compounds that had straight-chain O-H groups were easy to absorb water [29].

| Table 2. Molecular structure of the stamp ink. |
|-----------------------------------------------|
| Pyrocatechol | 4 Methyl Catechol | Phenol |
| ![Pyrocatechol](image1) | ![4 Methyl Catechol](image2) | ![Phenol](image3) |
| 2- Propanol, 1-Amine | Glyceraldehyd | Glycerol |

**The printing results of stamp ink**
The printing result of the stamp ink on a paper is in figure 6. The 25% FeSO\(_4\) treatment, having the lowest glycerol content of 3.75%, produced the best result, in terms of quality, on the paper. Its absorption capacity was low due to the low glycerol content, there producing clearer results compared with other treatments, as shown in figure 6. Visually, the resulting color matches those on the market today, namely purple. Stamp ink from gambier with Al\(_2\)(SO\(_4\))\(_3\) complexing produced a different color, namely redish yellow with a slightly faded appearance [14].

![Figure 6. The printed results from stamp ink with FeSO4 treatment.](image4)
4. Conclusion
Based on the results, the 25% FeSO₄ treatment was best for the stamp ink, which contained 11.44% pyrocatechol, 3.74% glycerol and 81.98% 2-propanol,1-amina. The printings on the papers were very clear and had a higher quality due to its low glycerol.

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