

HPLC-DAD IDENTIFICATION OF COMPOUNDS IN CORROSION INHIBITOR SALIX ALBA BARK EXTRACT AND THE HYDROLATE

Milica Zdravković^{1a}, Slađana Savić^{2b}, Vesna Grekulović^{1c}, Dalibor Stanković^{2d}

¹ Technical Faculty Bor, University of Belgrade, V.J. 12, 19210 Bor, Serbia

² Faculty of Chemistry, University of Belgrade, Studentski trg 16, Belgrade, Serbia

^{1a} mboskovic@tfbor.bg.ac.rs, 0000-0001-9488-9151

^{2b} sladjana@chem.bg.ac.rs, 0000-0002-1483-110X

^{1c} vgrekulovic@tfbor.bg.ac.rs, 0000-0001-6871-4016

^{2d} dalibors@chem.bg.ac.rs, 0000-0001-7465-1373

Abstract

The compounds present in *Salix alba* bark (SAB) extract and its hydrolate were identified using high-performance liquid chromatography with diode array detection (HPLC-DAD). SAB extract and its hydrolate were obtained by evaporating a macerate of dried, ground white willow bark and hot distilled water. A total of 19 standard polyphenolic compounds were used for the HPLC analysis. Results indicate that only 4-hydroxybenzoic acid (4-HBA) was detected in the SAB hydrolate. In contrast, both gallic acid and caffeic acid were present in the SAB extract. The presence of 4-HBA indicates the potential possibility of using SAB hydrolate as a starting component for the synthesis of parabens and other 4-HBA derivatives. Additionally, the identification of gallic and caffeic acids in the SAB extract further confirms the effect as a cathodic inhibitor of copper corrosion in chloride environments, because both acids are proven cathodic inhibitors of copper in different corrosion environments.

Keywords: white willow bark, HPLC, caffeic acid, gallic acid, 4-hydroxybenzoic acid

1. INTRODUCTION

Identification of compounds in herbal corrosion inhibitors is often performed using the HPLC method [1,2]. In this way, it is possible to determine which of the compounds have the greatest effect on corrosion inhibition, enabling a better understanding of the electrochemical properties and reaction mechanisms of corrosion inhibition processes [3]. Also, based on the compounds present, it is possible to additionally understand the complexity of inhibiting metal corrosion, especially when organometallic complexes occur between plant corrosion inhibitor molecules and metal ions due to corrosion processes [4]. The chemical structure and physicochemical properties of these compounds, like functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecules, should be considered [5,6]. The compounds present in the herbal corrosion inhibitor adsorb onto the metal surfaces, and thus protect them from the corrosive effect of the electrolyte [7].

Salix alba bark (SAB) extract, better known as white willow bark extract, has been identified as a cathodic type of corrosion inhibitor that exhibited protective properties against copper corrosion in chloride conditions (specifically, in a 0.5 M NaCl solution) [8]. However, the specific compounds in this extract remain unclear. It is well-known that white willow bark contains salicin, which acts as an effective corrosion inhibitor of some metals [9]. Furthermore, white willow is the main source of salicin and other salicylic derivatives - salicortin, 2'-O-acetylsalicortin, and tremulacin, that share structural similarities with aspirin (acetylsalicylic acid) [10].

The aim of this work is to identify the compounds in SAB extract and hydrolate using the HPLC method. This will help determine whether salicin or its derivatives function as corrosion inhibitors or if other compounds affecting copper corrosion are present. Hydrolate analysis was performed to determine the possible application of SAB hydrolate, which is a by-product of obtaining SAB

extract. By determining the potential application of SAB hydrolate, it is possible to achieve a circular process, considering that the residual plant material from willow bark can be used in biosorption and applications in the pulp industry [11].

2. EXPERIMENTAL

2.1 Preparation of white willow bark extract

SAB extract and hydrolate were obtained from a white willow bark macerate. This macerate was prepared by pouring hot distilled water over ground white willow bark. After filtration of the mixture on a Buchner funnel under vacuum, the filtrate was transferred to a rotary evaporator Buchi R-210. The solvent removal process was carried out at 72 mbar and 40 °C, resulting in a brown extract, which resembles resin, and the hydrolate.

2.2 Chemicals

A mixture of methanol (HPLC grade, Sigma Aldrich) and water (HPLC grade, Sigma Aldrich) in a 70/30 (v/v) ratio was used to dilute the extract prior to high-performance liquid chromatography with diode array detector (HPLC-DAD) analysis. Acetonitrile (eluent A, HPLC grade, Sigma Aldrich) and water (eluent B, HPLC grade, Sigma Aldrich) were used as mobile phases, both with 0.1 % of formic acid (HPLC grade, Fluka) in HPLC-DAD analysis. 4-Hydroxybenzoic acid, 4-hydroxyphenylacetic acid, aesculetin, apigenin, arbutin, caffeic acid, chlorogenic acid, ellagic acid, gallic acid, isorhamnetin, isorhamnetin-3-o-glycoside, kaempferol, kaempferol-3-o-glycoside, luteolin, neochlorogenic acid, p-coumaric acid, quercetin, quercetin-3-O-glycoside, and syringic acid were used as standard polyphenolic compounds.

2.3 HPLC analysis

The SAB hydrolate and extract were analyzed by the HPLC-DAD system (Thermo Ultimate 3000 RS, Germany), alongside the standards. Hydrolate and standards were filtered (0.22 µm syringe filters, PTFE membrane, 15 mm, Agilent Technologies) before HPLC-DAD analysis. The extract sample was weighed (0.0864 g) and diluted with methanol/water mixture up to 25 cm³, assisted by an ultrasound bath. This solution was then syringe-filtered, like the rest of the samples. The HPLC-DAD analysis was conducted as reported elsewhere [12], using the Chromeleon software, v6.8 (ThermoFisher Scientific, Germany) for instrument manipulation and data processing.

3. RESULTS AND DISCUSSION

3.1 HPLC profile of willow bark hydrolate and extract

The chromatographic profile of SAB hydrolate and extract are shown in Figure 1. The number and intensity of peaks clearly indicate that the extract has a more complex composition than the hydrolate [13]. Out of 19 screened polyphenolic compounds, only 4-hydroxybenzoic acid (4-HBA, retention time 12.4 min) was identified in the hydrolate sample (Figure 1A). This compound was not identified in the extract (Figure 1B), which had gallic acid (at 7.7 min) and caffeic acid (at 9.8 min).

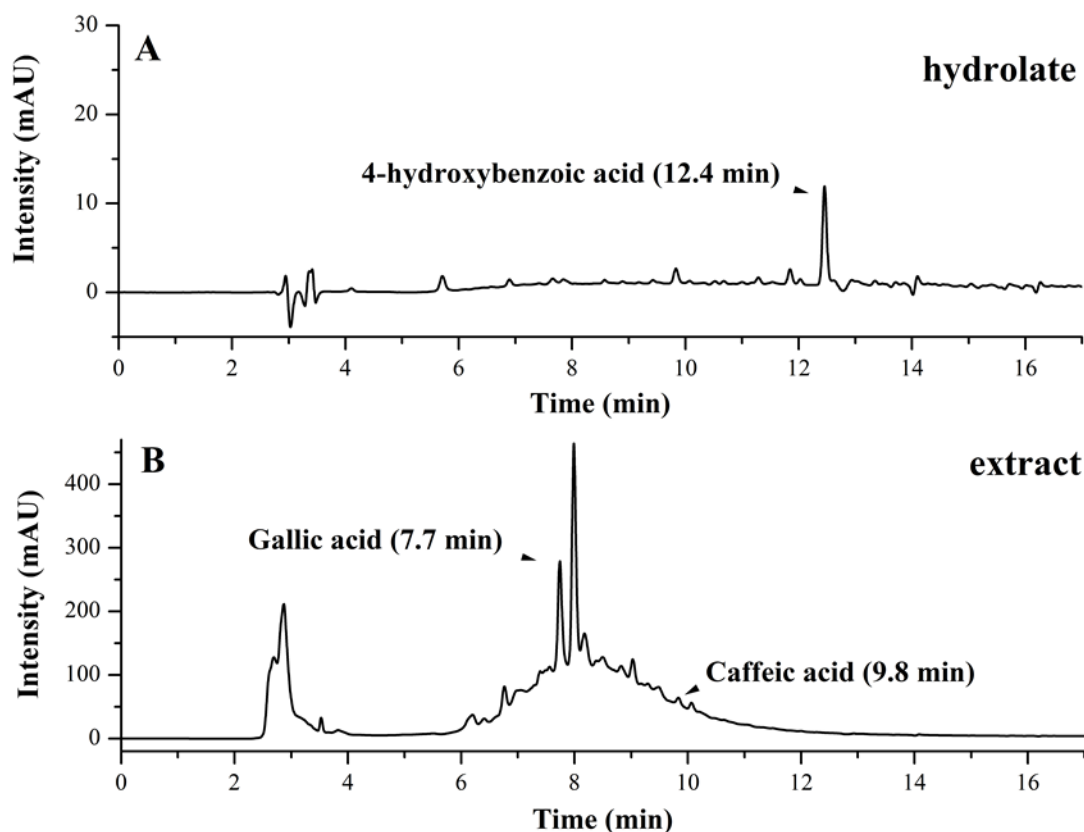


Figure 1. Chromatograms of willow bark hydrolate (A) and extract (B) at 254 nm

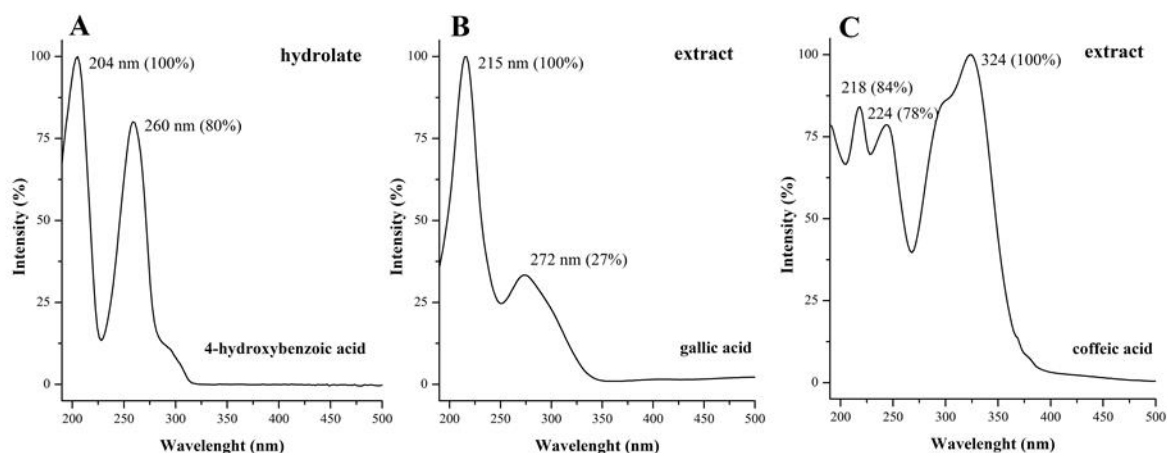
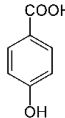
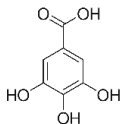
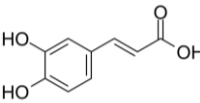


Figure 2. UV-Vis spectra of 4-hydroxybenzoic acid (A), gallic acid (B), and caffeic acid (C) from the corresponding chromatographic peaks at 254 nm

The typical UV-Vis spectra for the identified compounds are provided in Figure 2. Surprisingly, neither the extract nor the hydrolate showed evidence of quercetin and p-coumaric acid content [14,15,16], which was found in willow wood samples from Quebec by Brereton *et al.* using LC-MS analysis [14]. Other compounds, such as salicin and its derivatives, tannins, flavonoids, and various phenolic glycosides, were also anticipated, but were not detected due to lack of appropriate standards [14,17,18,19]. The content of polyphenolic compounds in SAB hydrolate and extract detected, based on their peak areas at 254 nm, is shown in Table 1.

Table 1. Content of polyphenolic compounds in SAB hydrolate and extract detected based on their peak areas at 254 nm

Sample name	Compound Name	Retention time (min)	Amount	Compound structure
SAB hydrolate	4-hydroxybenzoic acid (4-HBA)	12.4	1.22 mg/L	
SAB extract	gallic acid	7.7	18.88 g/kg	
SAB extract	caffeic acid	9.8	0.25 g/kg	

SAB hydrolate has not been chemically analyzed so far, However, the presence of 4-HBA enabled assessing its further use as a by-product in the extraction of SAB. Recent research has shown that various biosynthetic techniques have been developed for producing the 4-HBA and 4-HBA-based products. The 4-HBA is a promising intermediate for several value-added bioproducts with potential biotechnological applications (food, cosmetics, pharmacy, fungicides, etc.) [20]. Apart from its well-known application in the synthesis of parabens, it can also serve as a monomer for the synthesis of liquid crystalline polymers. This compound has various biological properties including hypoglycemic, anti-inflammatory, antiviral, and antioxidative activities [21,22].

Furthermore, SAB extract has demonstrated its effectiveness as an inhibitor of copper corrosion in chloride environments [8]. Its inhibitory effect is supported by the anti-corrosive properties of gallic and caffeic acid towards copper [23,24]. Wherein gallic acid may be considered to be a cathodic inhibitor that does not interfere directly with the cathodic process, but modifies the corrosive environment [23]. In addition to copper, gallic acid also acts as an aluminum and carbon steel corrosion inhibitor [25, 26]. Caffeic acid has also been shown to be an effective corrosion inhibitor of copper in 0.5 M NaCl solution and sulfuric acid, acting as a cathodic corrosion inhibitor [24, 27].

4. CONCLUSION

Using 19 standards polyphenolic compounds, the presence of compounds in the SAB extract and hydrolate was evaluated by the HPLC analysis. The chromatographic profile of the analyzed samples revealed that the SAB extract consisted of significantly more compounds compared to its hydrolate. In the hydrolate, only 4-hydroxybenzoic acid was confidently identified, whereas the presence of gallic and caffeic acid was confirmed in the extract. The presence of these components indicates the possibility of using SAB hydrolate as a starting component for synthesis, while SAB extract may be used as an effective metal corrosion inhibitor.

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