Journal of Chromatography & Separation Techniques

OPEN ACCESS Freely available online

Mini Review

# LC-MS Characterization and Evaluation as Corrosion Inhibitor of the Aqueous Extract of *Ziziphus joazeiro* Stem Bark

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## ABSTRACT

The aqueous Extract of Joazeiro Stem Bark (EJSB) was chemically characterized by Liquid Chromatography-high resolution Mass Spectrometry (LC-MS) and examined as potential corrosion inhibitors of mild steel in 1 mol $L^{-1}$ hydrochloric acid media, using weight-loss measurements. The LC-HRMS analysis revealed compounds already present in the *Ziziphus joazeiro*. The chemical characterization of ECCJ by LC-MS analysis enabled the identification of 18 compounds. Among the compounds detected, saponins were noted as the main constituents that had the specific characteristics needed to adsorb on the metal surface and to form a protective film. Varying the concentration of the inhibitors from 100 mg $L^{-1}$ to 800 mg $L^{-1}$, the results show an increase in anticorrosive efficiency from 85.4 to 89.8 for EJSB, using the data of the gravimetric essay. Considering that the saponin molecules, the main constituent from jua, are responsible for its inhibitory action.

**Keywords:** *Ziziphus joazeiro* stem bark extract; Corrosion inhibitor; Mild steel; LC-MS; Electrochemical measurements

## INTRODUCTION

*Ziziphus joazeiro* is a tree native to the Brazilian semiarid region, in the caatinga biome, where it is popularly called "Juazeiro". It has economic potential for the hinterlands of Northeastern Brazil, being used for ornamentation purposes, as an energy source, as popular medicines, for production of cosmetic products and human and animal food, mainly during droughts [1]. Regarding the chemical composition of the *Ziziphus joazeiro* aqueous stem bark, steroids and saponins were reported as being the major constituents together with flavonoids [2,3]. Saponins are a class of compounds structurally characterized by the presence of a steroid-like glycoside. These saponins are produced by the plant's secondary metabolism and has been reported as corrosion inhibitors. They have a good corrosion inhibition effect for mild steel in acidic medium (HCl or $H_2SO_4$) [4,5]. Since chemical properties should be the first step to understand some corrosion-inhibitory properties for natural compounds, we first determined the chemical profile of the aqueous Extract of *Ziziphus joazeiro* Stem Bark (EJSB) and then investigated its inhibitory action.

## LITERATURE REVIEW

The chemical characterization of EJSB was carried out by Liquid Chromatography-Mass Spectrometry (LC-MS). The EJSB samples (n=3) were dissolved in acetonitrile:water (1:1 v/v) and diluted to 1.0 mg $mL^{-1}$ in acetonitrile:water (3:7 v/v) before analysis. The LC-MS analysis was performed in a hybrid quadrupole-orbitrap high-resolution mass spectrometer (Q Exactive Plus, Thermo Scientific, Frenton, CA, USA). The source parameters were spray voltage 3.9 kV (ESI+) and 3.6 kV (ESI-), capillary temperature 300°C, source temperature 380°C, S-lens RF level 50, sheath and auxiliary gases 45 and 15 arbitrary units, respectively. Data were obtained in full-scan mode over the m/z range of 120-1000, using a resolution of 35,000 followed by data-dependent MSMS experiment at a resolution of 17,500 and stepped normalized collision energy of 15%-45%. Sample components were separated in a reversed-phase C18 column (Thermo hypersil gold 150 mm × 2.1 mm; 3.0 µm particle size) using an Ultimate 3000 UHPLC system (Thermo Dionex, Thermo Scientific, Frenton, CA, USA). Mobile phase A was 0.1% formic acid and 5 mmol $L^{-1}$ ammonium formate in water and mobile phase B was 0.1% formic acid in acetonitrile. The chromatographic separation was performed in gradient elution

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**Received:** 16-Nov-2021, Manuscript No. JCGST-21-14422; **Editor assigned:** 19-Nov-2021, PreQC No. JCGST-21-14422 (PQ); **Reviewed:** 03-Dec-2021, QC No. JCGST-21-14422; **Revised:** 02-Mar-2023, Manuscript No. JCGST-21-14422 (R); **Published:** 30-Mar-2023, DOI: 10.35248/2157-7064.23.14.517

**Citation:** Mauro AC (2023) LC-MS Characterization and Evaluation as Corrosion Inhibitor of the Aqueous Extract of *Ziziphus joazeiro* Stem Bark. J Chromatogr Sep Tech. 14:517.

mode at a flow rate of 0.35 mL $min^{-1}$ as follows: 0-1 min 5% B, 1-16 min 95% B, 16-18 min 95% B, 18-22 min 5% B. The injection volume was 8 µL and the column temperature was 40°C. The raw data files from the EJSB samples and the sample solvent blank injection were converted to them zXML format into pairs for negative and positive ionization modes. Those files were then imported into MZMine2 for data processing to generate an aligned feature list across their MS/MS and chromatographic separation for each polarity [6]. From the MZMine2, the exported .mgf aligned feature list for each polarity were submitted to the GNPS web server for Feature-Based Molecular Network (FBMN) analysis; then, their results were submitted to the GNPS [7].

The resulting network was plotted using the Cytoscape software. Concomitantly, those same .mzXML files were submitted to LipidXplorer for screening of expected saponinsas they are considered to be the main secondary metabolite from the *Zyziphus* species, using the same protocol described elsewhere. The results yielded by this last application were manually combined with the molecular network yielded by the GNPS workflow for annotation. Besides, compound annotation was also performed by comparing the experimental MS/MS spectra from compounds in the extract to those available in the NIST MSMS 2014 library and Mass Spectra of North America (MoNA).

## DISCUSSION

A total of 6 compounds were annotated in the samples by comparing their MS/MS spectra and exact mass measurement (error<6 ppm), using the public (MoNA) and commercial (NIST MSMS 2014) databases in MS-DIAL software: Agmatine (tR 0.7 min, $[M+H]^+$, error 2.4 ppm), aspartic acid (tR 0.8 min, $[M+H]^+$, error 4.7 ppm), gluconic or galactonic acid (tR 0.8 min, $[M-H]^-$, error 5.1 ppm), citric or isocitric acid (tR 0.8 min, $[M-H]^-$, error 4.0 ppm), N-acetylglutamic acid (tR 0.9 min, $[M+H]^+$, error 4.6 ppm), 3-Hydroxy-11-ursen-28,13-olide (tR 10.5 min, $[M+H-H_2O]^+$, error 1.9 ppm). Most of them are highly polar compounds eluted at the beginning of the chromatographic analysis in the reversed-phase column. The LC-MS datasets from ESI-(+) and ESI-(-) analyses were submitted to the FBMN for visualization of the chemical space of EJSB. Among the compounds detected, triterpenes and saponins were annotated as major constituents. GNPS did not yield any match with its database [8]. The Lipid XPlorer approach enabled the annotation of 12 derivatives of cucurbitacins and jujubogines aglycones and glycosides. It is virtually impossible to determine the unequivocal structure of each compound without laborious purification procedures, but it is safe to say there is a broad range of compounds with similar structure composition at different hydroxylation stages due to the number of nodes and the common $H_2O$ neutral loss of 18.01 Da [9]. The fragmentation pattern widely shared by the compounds within this network is in agreement with such structures closely related to the jujubogenin and pseudojujubogenin with fragments at m/z 121.10, 201.1 and 315.23. Thus, sharing the same network, many compounds were annotated as mono bi- and tri-glycoside derivatives due to neutral loss of the characteristic molecular weight of pentose, and hexone of 132.04 and 162.05 Da, respectively.

The weight loss essays were performed according to norm ASTM G31-7. Inhibition Efficiency (IE%) was obtained through Equation (1):

$$EI = \left[\frac{(W_{corr,0} - (W_{corr})}{W_{corr,0}}\right] x\ 100 \quad (1)$$

where $W_{corr,0}$ is the corrosion rate (g $cm^{-1}$ $h^{-1}$ ) in the absence of the inhibitor and $W_{corr}$ is the corrosion rate in the presence of the inhibitor.

The evaluation of the aqueous Extract of Joazeiro Stem Bark (EJSB) as corrosion inhibitors for AISI 1020 carbon steel in 1 mol $L^{-1}$ HCl medium using gravimetric assays, indicated that the evaluated are promising, reaching maximum efficiency of 89.0% for the ECCJ. This suggests a protection mechanism due to the adsorption of molecules from the *Ziziphus Joazeiro* stem bark on the metal surface.

## CONCLUSION

The aqueous Extract of Joazeiro Stem Barks (EJSB) act as a great corrosion inhibitor in an acid medium of 1 mol $L^{-1}$ HCl. The chemical characterization of the EJSB by LC-MS analyses made the identification of 18 compounds possible. Among the compounds detected, saponins were annotated as major constituents which have structural characteristics necessary to adsorb on the metal surface and form a protective film. Considering the saponins as major constituent in EJSB, it is possible to suggest that they should be responsible for the adsorption process.

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