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Surface enhanced Raman scattering study of the antioxidant alkaloid boldine using prismatic silver nanoparticles



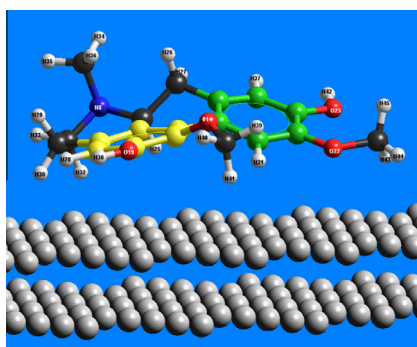
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HIGHLIGHTS

- The SERS spectrum of the antioxidant alkaloid boldine has been registered.
- Spectral SERS reproducibility is obtained by using of prismatic silver nanoparticles.
- Theoretical calculations predict the orientation of boldine onto the Ag surface.

GRAPHICAL ABSTRACT



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ABSTRACT

Prismatic silver nanoparticles (PNPs) were used in the surface enhanced Raman scattering (SERS) study of the antioxidant alkaloid boldine (5,6,6a,7-tetrahydro-1,10-dimethoxy-6-methyl-4H-dibenzo[de,g]quinoline-2,9-diol). Prismatic and quasi-spherical (QsNPs) silver nanoparticles were synthesized and characterized by UV–Vis spectra, topographic profile (AFM) and zeta potential measurements. Raman and infrared (IR) spectra of the boldine were registered. Theoretical model calculations of the boldine onto the Ag surface predict a nearly coplanar orientation of the benzo[de]quinoline moiety and non-bonded interactions (electrostatic).

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Introduction

The boldo (*Peumus boldus*) is an endemic tree from Chile. The boldo leaves extract is of great interest to pharmaceutical industry, as it possesses high antioxidant activity due to its content of flavonoids and alkaloids. Boldine (5,6,6a,7-tetrahydro-1,10-dimethoxy-6-methyl-4H-dibenzo[de,g]quinoline-2,9-diol) is an aporphine alkaloid, associated with biological activities such as anti-tumor

promoting, anti-inflammatory and antipyretic [1]. Boldine protect fish oil against thermal peroxidation displaying an activity similar to that of the quercetin flavonoid [2].

Different alkaloids have been studied by Raman and IR techniques, and computational calculation methods. Baranska et al. [3] studied the tobacco alkaloids (nicotine, normicotine, cotinine, anabasine) using Raman spectroscopy and supported by Density Functional Theory (DFT) calculations at the B3LYP/aug-cc-pVDZ level of theory; for all tobacco alkaloids the characteristic Raman bands were assigned. A vibrational analysis was performed on the molecular structure of boldine hydrochloride using QM/MM

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[4]; geometry, harmonic vibrational frequencies and IR intensities were calculated by QM/MM method with B3LYP/6-31G(d) and universal force field (UFF) combination using the ONIOM code. Srivastava et al. [5] studied by IR, Raman and quantum chemistry the structural and spectral characteristics of boldine; electrostatic potential surface, optimized geometry, harmonic vibrational frequencies, IR intensities and activities of the Raman scattering were calculated by *ab initio* Hartree–Fock (HF) and DFT, employing B3LYP with a complete relaxation in the potential energy surface using the 6-311G(d,p) basis set.

The Raman spectral signal intensity is dramatically enhanced from a determined analyte–metal nanoparticle interaction, giving rise to the surface-enhanced Raman scattering (SERS); this technique has been applied to the detection of drugs, pesticides, explosives, and in the identification of nanostructures, biosensors, tumors and cancer cells. Cañamares et al. [6] studied the protuberberine alkaloids (palmatine, jatrorrhizine, and coptisine) by using SERS in combination with DFT calculations. The SERS of boldine has not been reported, probably due to the antioxidant properties which could induce high reactivity with the metal nanoparticles, avoiding obtaining a reproducible SERS spectrum. A SERS study of quercetin and related flavonoids was reported [7], showing chemical changes in the quercetin structure. Jurasekova et al. [8] demonstrate that the interaction of the quercetin with silver nanoparticles (prepared by reduction with citrate) and metal ions (Cu(II), Zn(II), Ag(I)) produces the formation of chelates as a result of the oxidation of the flavonoid, involving successive polymerization.

The aim of the present contribution deals with the preparation and characterization of prismatic (PNps) and quasi-spherical Ag nanoparticles (QsNps) for the SERS study of boldine (prepared by reduction with borohydride). The SERS of boldine has not been reported, probably due to the antioxidant properties which could induce high reactivity with the metal nanoparticles, avoiding obtaining a reproducible SERS spectrum. The spectral assignment of the SERS data is supported on our own Raman data; the analyte metal surface interaction nature is analyzed from the SERS band analysis of the hydroxyl group and the theoretical calculations of a molecular model for the boldine interacting with the Ag surface.

Experimental

Samples

Solid boldine, with a purity of 99.2% was used without further purification. The structure of boldine is shown in Fig. 1. The following chemicals were used for the preparation of the nanoparticle colloidal solutions: tri-sodium citrate dihydrate (99%, Merck), silver nitrate 99.9999% metal basis (Aldrich), hydrogen peroxide 30% (Merck), potassium bromide (FT-IR grade >99%, J.T. Baker Chemicals), and sodium borohydride (Merck GR for analysis). All chemicals were used as received.

Colloids preparation

Silver prism colloids were prepared following Frank et al. [9]. Some modifications to the reference procedure were performed, in particular, the time prior to the addition of the reducing agent standard solutions were prepared using ultrapure water 0.055 $\mu\text{S}/\text{cm}$ conductivity: 1.25×10^{-2} M tri-sodium citrate, 3.75×10^{-4} M silver nitrate, 5.0×10^{-2} M hydrogen peroxide, 1.0×10^{-3} M potassium bromide and 5.0×10^{-3} M sodium borohydride (reducing agent). To six 20 mL Pyrex test tubes, the following reagents were added in the order: 2.0 mL of 1.25×10^{-2} M sodium citrate, 5.0 mL of 3.75×10^{-4} M silver nitrate, and 5.0 mL of 5.0×10^{-2} M H_2O_2 . Then,

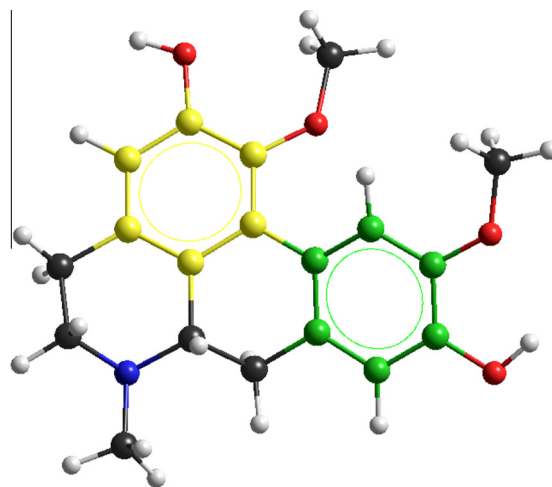


Fig. 1. The structure of boldine. The benzo[de] and benzo[g] quinolinic rings are represented by yellow and green colors, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

to each vial a different volume of 1.0×10^{-3} M KBr was added as follows: 0, 10, 15, 20, 25 and 40 μL . To start the synthesis step, 2.5 mL of freshly prepared 5.0×10^{-3} M sodium borohydride were added within no more than 10 min after preparation. Then, the solution was abruptly and totally added to each vial under simultaneous stirring. Once all reagents were combined, the caps were placed on the vials and they were carefully swirled using a Vortex mixer during about 2 min. The progression of the reaction becomes evident through the visual changes consistent with the morphological modification from the quasi-spherical to prismatic and growing of the silver nanoparticles. Typically, the sequence of color changes from yellow to orange to red to purple to violet to blue to pale greenish blue for the largest nanoprisms. It takes approximately 3 min to reach a stable color. The size and shape of the nanoparticles are controlled by the KBr addition which induces halt of the process. Fig. 2 displays the colloidal solutions from blue (0 μL) to yellow (40 μL) obtained by increasing the KBr concentration. In order to increase the PNps nanoparticles concentration, 1.5 mL of the PNps colloidal solutions were centrifugated at 10,000 rpm during 30 min; 1 mL of the supernatant was extracted. 0.5 mL of the solution was used for the SERS experiments.

Colloids characterization

UV–Vis–NIR extinction spectra of the six colloidal solutions display maxima at 714, 681, 681, 502, 495 and 424 nm, see Fig. 3. The



Fig. 2. Colloidal solutions from yellow to blue obtained by dilution of the KBr solution (2.75×10^{-6} , 1.72×10^{-6} , 1.38×10^{-6} , 1.03×10^{-6} , 6.90×10^{-7} , 0.0 M). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

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