Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 133 (2014) 1–6

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Synthesis, structural analysis, theoretical studies of some lawsone derivatives

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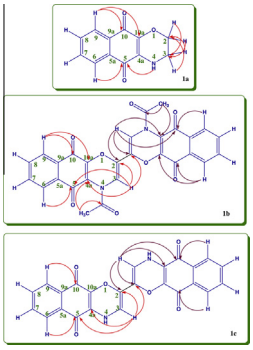
HIGHLIGHTS

- Lawsone derivative compounds are synthesized.
- Structures of the compounds are analyzed by FT-IR, Mass, Elemental analysis, ^{1}H, ^{13}C, HSQC, HMBC.
- Theoretical studies are done by Gaussian-03 using the Hartee–Fock method and Basis Set 3-21G.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 1 February 2014
Received in revised form 4 May 2014
Accepted 9 May 2014
Available online 28 May 2014

Keywords:
Lawsone derivatives
Green synthesis
HOMO–LUMO
Spectral analysis

ABSTRACT

A series of lawsone derivatives are synthesized. The structures of the synthesized compounds are analyzed by FT-IR, Mass, Elemental analysis, ^{1}H, ^{13}C, HSQC, HMBC and theoretical studies.

Introduction

Naturally occurring quinones have several different roles in organisms, they are functional constituents of several biochemical systems (e.g. ubiquinones and vitamin K1). 2-Hydroxy-1,4-naphthoquinone (Lawsone) is the principal natural dye in the leaves of henna, *Lawsonia inermis*. Henna has been used more than 4000 years not only as a hair dye, but also as a body paint and tattoo dye. Today, semi permanent hair dyes containing Henna as well as its pure dye ingredient are widely used and have become increasingly popular due to their natural origin [1]. Lawsone was first isolated from the leaves of *Lawsonia inermis* L. In 1959 [2], lawsone and related compounds have been reported to possess interesting biological activities such as antitumor, antibacterial and antifungal properties [3–5]. It is also used as a hair dye [6] and use an ultra-violet (UV) filter in sunscreen formulation [7]. Naphthoquinones constitute one of the largest and diverse groups of plant secondary metabolites with a broad range of properties [8,9] antifeedent [10] and allelopathic activity [11] which contribute to plant defense. They also possess important pharmacological activities, such as antioxidant [12], antiinflammatory [13], and anticancer [14]. With nearly one-third of the global population

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http://dx.doi.org/10.1016/j.saa.2014.05.037
1386-1425/

infected by Mycobacterium tuberculosis (MTB), tuberculosis (TB) is still a major cause of death. Indeed, in 2006 over nine million new cases and 1.7 million deaths occurred due to TB, and there is now a significant concern about the emergence of multi-drug resistant (MDR) strains of TB with an estimated 0.5 million cases worldwide [15].

However, the nature of many biological properties of lawsone and its derivatives are remains unclear, therefore the investigation of the structure and reactivity of this prolific medicinal agent is important for organic chemists. In the present work, we have summarized a comprehensive study of the lawsone derivatives and its molecular structure was analyzed by 1D and 2D NMR spectroscopy, Mass, Elemental analysis. Theoretical calculations were carried out by using Gaussian-03 program [16,17].

Results and discussion

The NMR and theoretical technics are powerful to confirm the synthesized compounds and special arrangement of the atoms of the compounds (optimized structures).

The lawsone derivatives **1a**–**5a** is synthesized with excellent yields by the reaction of substituted lawsone with ethanol amine in water (Scheme 1) [18]. Then the compound **1a** is reacted with acetic anhydride gives unexpected dinner product along with the acetylation **1b** (Scheme 2) [18] also checked the compound **1a** with chloroacetyl chloride, it gives the only unexpected dinner product **1c** without chloroacetylation (Scheme 3) [18]. The reaction time, the yields and the substitutions (–R) of the synthesized products are given in (Table 1). The structures of the all synthesized compounds **1a–5a**, **1b**, **and 1c** are confirmed by FT-IR, ^{1}H NMR, ^{13}C NMR, HSQC, HMBC, Mass spectral studies and elemental analysis. Melting point, FT-IR and elemental analysis data for the all synthesized compounds are given in the supplementary data (Table 2).

In order to determine the structures of the synthesized compounds, compound **1a, 1b, 1c** is taken as the representative compounds. Structures of representative compounds and HMBC correlations are shown in Fig. 1.

*Infrared spectral analysis of representative compounds **1a**, **1b**, **1c***

The FT-IR spectrum of compound **1a** shows characteristic absorption frequencies appeared at 3352 cm^{-1} due to aromatic CH stretching vibrations. The absorption bands around 2923–2843 cm^{-1} due to the aliphatic CH stretching vibrations. The absorption band at 1674 cm^{-1} is assigned to carbonyl stretching vibration. The absorption band at 3428 cm^{-1} is assigned to NH stretching vibration. Compound **1b** shows characteristic absorption frequencies around 3101 cm^{-1}, 3038–2849 cm^{-1}, 1761 cm^{-1} respectively as compound **1a** and it does not show the NH stretching frequency. The absorption bands of compound **1c** 3073 cm^{-1}, 2924–2849 cm^{-1}, 1678 cm^{-1} and 3174 cm^{-1} are also similar to the compound **1a** The FT-IR spectra of all synthesized compounds **1a–5a**, **1b** and **1c** are shown in the supplementary data (Figs. 2–8).

*^{1}H NMR spectral analysis of **1a***

In the ^{1}H NMR spectrum of compound **1a**, the H2 protons attached to the oxygen observed as a triplet at 3.59 ppm. A triplet observed at 2.88 ppm is due to the H3 protons attached to the nitrogen. The NH proton H4 absorbed as a singlet at 5.44 ppm. The aromatic protons are absorbed in the range of 7.52–7.78 ppm.

*^{1}H NMR spectral analysis of **1b***

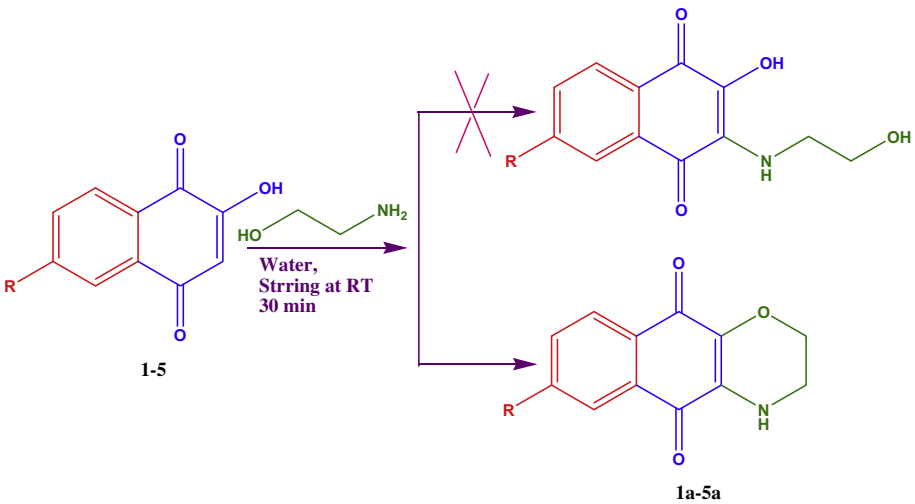
In the ^{1}H NMR spectrum of compound **1b**, the singlet observed at 7.04 ppm is due to the H3 proton attached to the nitrogen. The acetyl methyl protons are absorbed as a singlet at 2.37 ppm. The aromatic protons are absorbed in the range of 7.89–8.04 ppm.

*^{1}H NMR spectral analysis of **1c***

In the ^{1}H NMR spectrum of compound **1c**, the singlet observed at 6.17 ppm is due to the H3 proton is attached to the nitrogen. The NH proton H4 absorbed as a singlet at 11.72 ppm. Aromatic protons are absorbed in the range of 7.79–8.01 ppm. Supplementary data (Figs. 9–15) shows the ^{1}H NMR spectra for the compounds **1a**–**5a**, **1b** and **1c**.

*^{13}C NMR spectral analysis of **1a***

In the ^{13}C NMR spectrum of compound of **1a**, ^{13}C resonate at 57.63 ppm is due to the C2 carbon attached to the oxygen and the 41.26 ppm is due to the C3 carbon attached to the nitrogen. The ^{13}C resonate at 171.81 ppm is due to the ipso carbon C4a attached to the nitrogen and the ^{13}C resonate at 106.83 ppm is due to the C10a carbon which is attached to the oxygen. The two signals observed at 186.94 ppm, 180.94 ppm are due to the two carbonyl carbons C5 and C10 respectively. The aromatic carbons resonated at in the range of 124.75–135.42 ppm.



Scheme 1. Synthetic route for compounds **1a**–**5a**.