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Syntheses, characterization and fluorescent properties of two series of dehydroabietic acid C-ring derivatives

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ABSTRACT

Two series of dehydroabietic acid C-ring derivatives, nitrogen-containing heterocycles (**6a**–**9b**) and C-12 substituted compounds (**10a**–**11b**), were synthesized and characterized by element analysis, IR, NMR and MS. The UV–vis absorption and fluorescence spectral characteristics of these compounds have been comparatively investigated, and their fluorescence quantum yields were further evaluated. Compared to dehydroabietic acid **1**, the absorption and emission spectra of these compounds were bathochromically shifted due to the multiple aromatic rings with rigid planar structures or the larger conjugation of benzene moiety.

1. Introduction

Dehydroabietic acid **1**, the main component of disproportionated rosin, can be easily obtained by catalytic dehydrogenation of abietic type resin acids or readily isolated from disproportionated rosin. It possesses aromatic diterpene structure with three ring, three chiral carbon atoms and a reactive carboxy group. Owing to its availability and unique structure, a considerable interest has been devoted to this compound as a starting material for the synthesis of many important multifunctional derivatives, such as antioxidants [1], antiviral substances [2], natural active drugs [3], chiral catalysts [4] and chiral surfactants [5].

Our previous work [6] has demonstrated that dehydroabietic acid derivatives can be a useful tool in the synthesis of chiral fluorescence derivatizing reagents. The potential of dehydroabietic acid derivatives [6], and the well known fluorescence properties of phenazines [7], quinoxalines [8], naphthalimides [9], biphenyl and polycyclic aromatic hydrocarbons as fluorescent chromophores, led us to construct these chromophores fused to the aromatic ring of the dehydroabietic acid skeleton. There seemed a good possibility that the new derivatives would show good spectral characteristics. In order to obtain some new dehydroabietic acid C-ring derivatives with strong emission property, several nitrogen-containing heterocycles, such as phenazines, quinoxalines and naphthalimides, incorporated into ring C, and some C-12 substituted derivatives were designed and synthesized. The UV–vis absorption and fluorescence spectra and fluorescence quantum yields for these compounds were measured in methanol. The structures of the starting material (dehydroabietic acid **1**) and the intermediates (compounds **2**, **3**, **4**, **5**) were depicted in Fig. 1. The synthetic routes of nitrogen-containing heterocycles (**6a**–**9b**) and C-12 substituted derivatives (**10a**–**11b**) were outlined in Scheme 1 and Scheme 2, respectively.

2. Experimental

2.1. General information

Melting points were determined in a WRS-1A melting point apparatus and are uncorrected. The spectra of ^{1}H NMR and ^{13}C NMR were measured in $CDCl_3$ on a Bruker AVANCE-500 MHz NMR spectrometer with TMS as internal standard. IR spectra were recorded on a Nicolet ESP 360 FT-IR instrument. The mass spectra were obtained on a BRUKER ESQUIRE HCT spectrometer. Elemental analyses were performed on a Carlo Erba model 1106 elemental analyzer. UV–vis absorption spectra were recorded with a CARY 100 spectrophotometer. Fluorescence spectra were collected with a RF-5301PC spectrophotometer at room temperature. The fluorescence quantum yields (Φ_f) were measured using quinine sulfate ($\Phi_f = 0.546$ in 0.5 mol/l H_2SO_4) [10] as the standard. Thin layer chromatography (TLC) was performed using TLC plates F254 and the compounds visualized by illumination under UV

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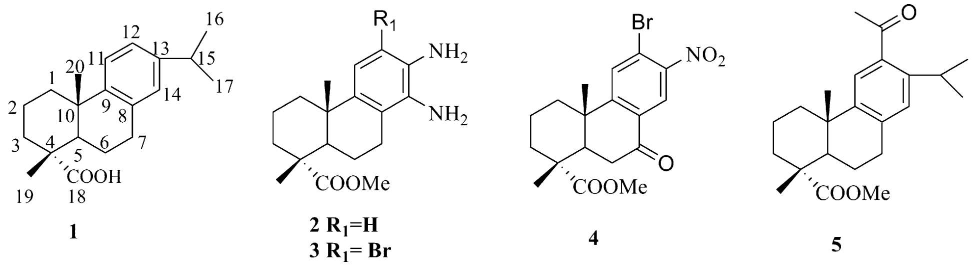


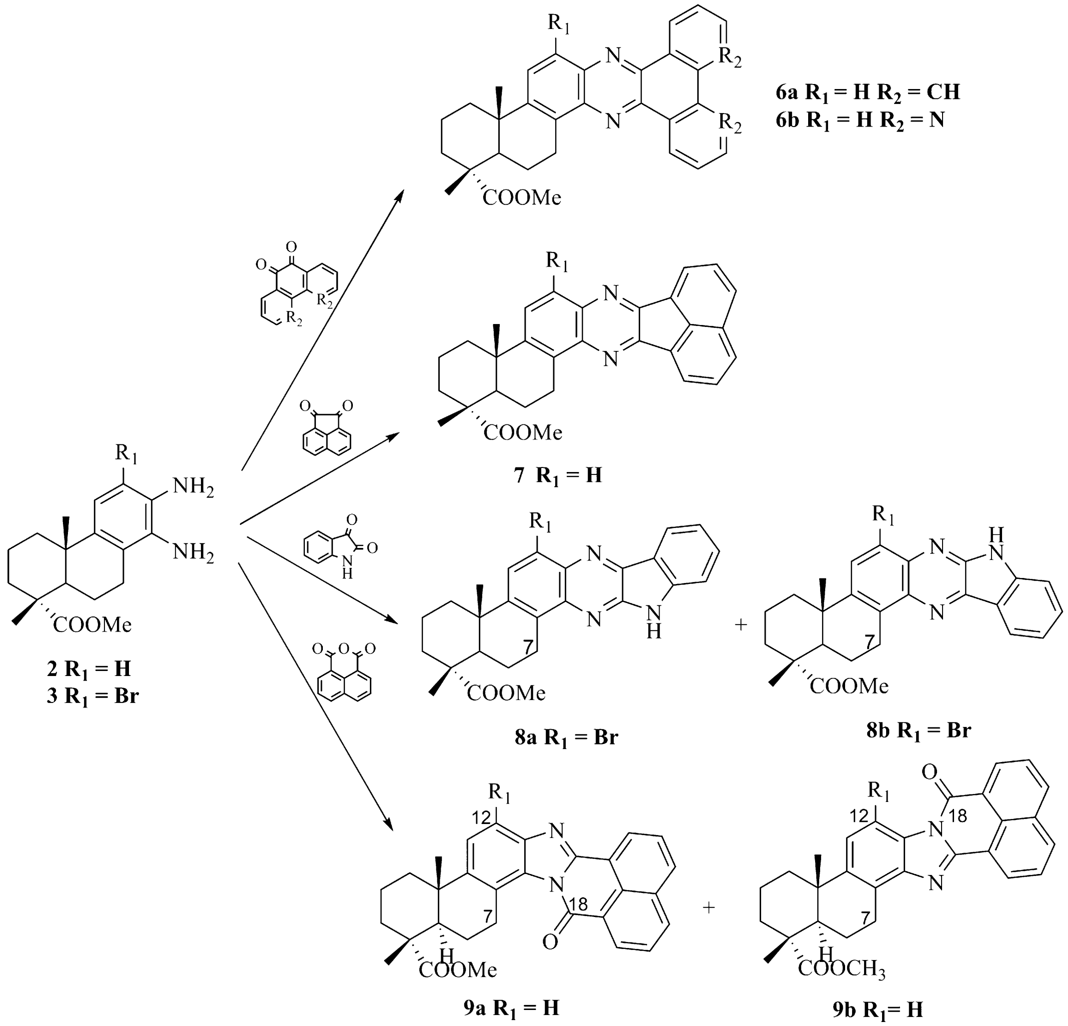
Fig. 1. Structures of dehydroabietic acid **1** and the intermediates **2**–**5**.

light at 254 nm. Silica gel used for column chromatography was 300–400 mesh.

The starting material, dehydroabietic acid **1**, was obtained from commercially disproportionated rosin and purified by repeated crystallisation of the ethanolamine salt [11]. The intermediates, i.e. methyl 13,14-diaminodeisopropyldehydroabietate **2** [1], methyl 12-bromo-13,14-diaminodeisopropyldehydroabietate **3** [1], methyl 12-bromo-13-nitro-7-oxo-dehydrodeisopropylabietate **4** [12], methyl 12-acetyldehydroabetate **5** [13] and 1,10-phenanthroline-5,6-dione [14] were prepared according to literature procedure. Reagents and solvents were of the purest grade available, dried and purified when necessary by standard procedures.

2.2. *Preparation of* ***6a***–***6b***

Methyl 13,14-diaminodeisopropyldehydroabietate **2** (400 mg, 1.3 mmol) in 10 ml ethanol was added dropwise to the solution of phenanthrenequinone (291 mg, 1.4 mmol) in 20 ml glacial acetic acid. The mixture was refluxed with stirring under nitrogen for 4 h (TLC monitoring). After cooling, the mixture was poured into 200 ml of ice-water, and a yellow precipitate was formed. The solid was filtered and purified with re-crystallization from ether/methanol (1:1), 440 mg (82.9% yield) of yellow crystals of the compound **6a** was obtained. m.p. 216.8–217.9 °C; ^{1}H NMR (CDCl$_3$, 500 MHz) δ: 9.41 (m, 2H), 8.58 (t, J = 8 and 4 Hz, 2H), 8.12 (d, J = 9 Hz, 1H), 7.84 (d, J = 9.5 Hz, 1H), 7.81–7.74 (m, 4H), 3.93 (dd, J = 18.5 and 6 Hz, 1H),



Scheme 1. The synthetic routes of dehydroabietic acid-based phenazines, quinoxalines and naphthalimides **6a**–**9b**.