Spectrochimica Acta Part A 76 (2010) 328–335

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

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

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

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ARTICLE INFO

Article history:
Received 15 November 2009
Received in revised form 23 February 2010
Accepted 15 March 2010

Keywords:
Dehydroabietic acid
Absorption
Fluorescence
Quantum yields

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 (Φ_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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doi:10.1016/j.saa.2010.03.014

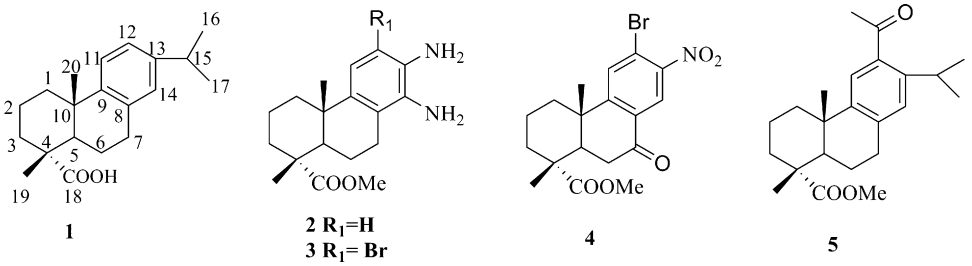


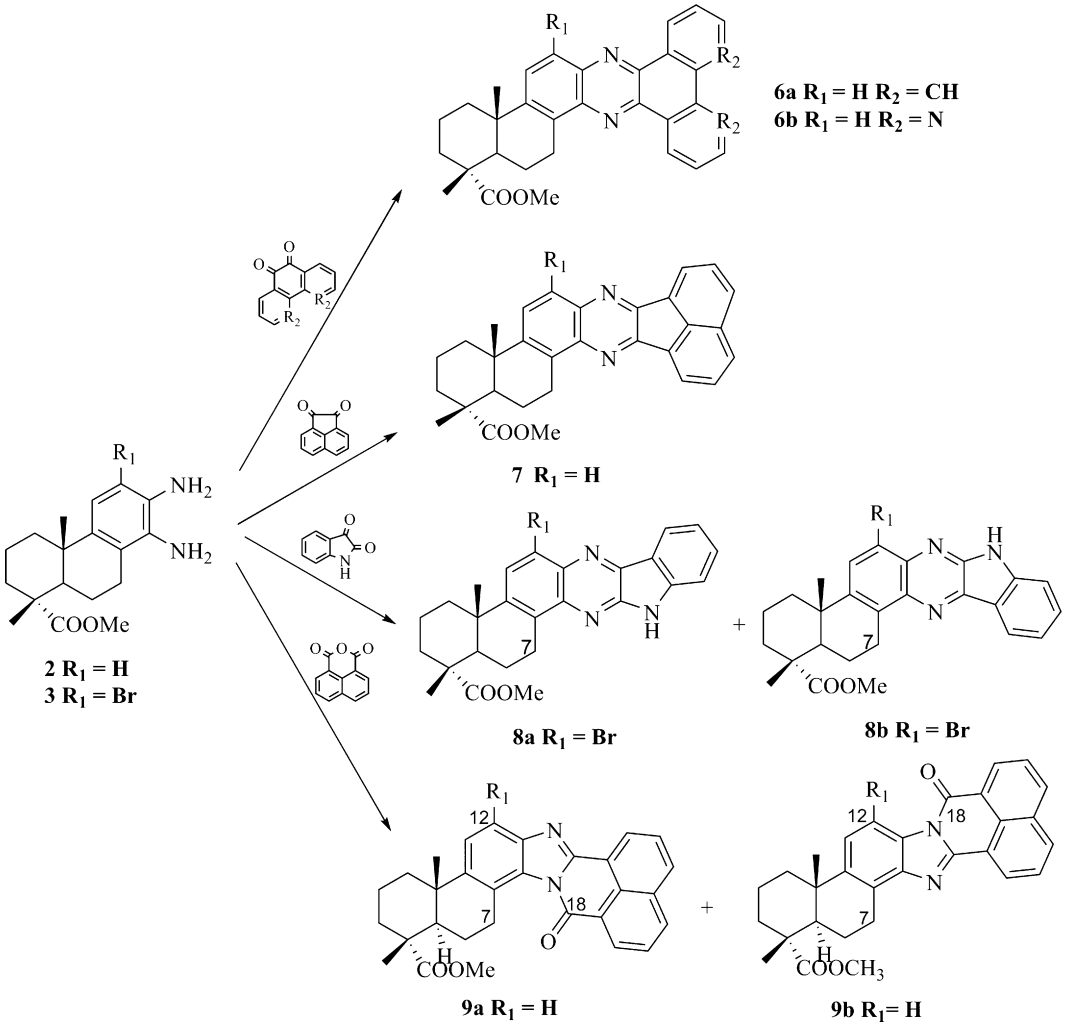
Fig. 1. Structures of dehydroabietic acid **1** and the intermediates **2**–**5**.

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

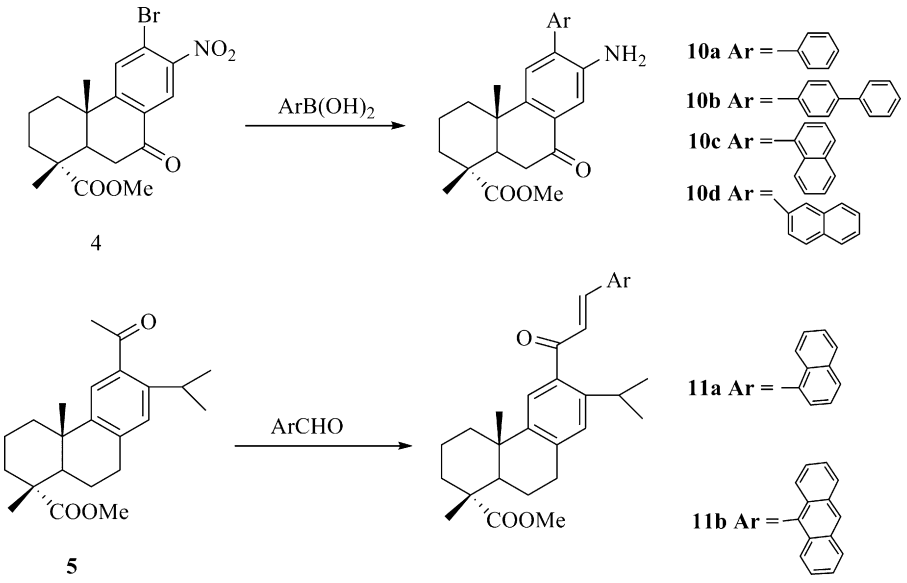
The starting material, dehydroabietic acid **1**, was obtained from commercially disproportionated rosin and purified by repeated crystallisation of the ethanolamine salt [11]. The intermediates, i.e. methyl 13,14-diaminodeisopropyldehydroabietate **2** [1], methyl 12-bromo-13,14-diaminodeisopropyldehydroabietate **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**.



Scheme 2. The synthetic routes of C-12 substituted derivatives **10a**–**11b**.

3.76 (s, 3H), 3.54 (m, 1H), 2.47–2.50 (m, 2H), 2.04–1.83 (m, 4H), 1.74–1.78 (m, 2H), 1.65 (m, 1H), 1.42 (s, 3H), 1.41 (s, 3H); ^{13}C NMR ($CDCl_3$ 125 MHz) δ: 179.0, 149.7, 144.1, 142.5, 140.6, 133.3, 131.9, 131.8, 130.9, 130.5, 129.8, 129.6, 127.8, 127.7, 127.6, 126.9, 126.1, 126.0, 122.8, 52.0, 47.8, 45.3, 45.1, 37.9, 37.8, 36.5, 26.0, 25.8, 24.4, 21.4, 18.6, 16.5; IR (KBr, cm^{-1}): 3066, 2929, 1714, 1449, 1360, 1246, 1113, 1034, 758, 724; anal. calcd for $C_{32}H_{30}N_2O_2$, C, 80.98; H, 6.37; N, 5.90; found: C, 80.90; H, 6.38; N, 6.08; MS (FAB): 475 (M^++1).

1,10-Phenanthroline-5,6-dione (300 mg, 1.4 mmol) was dissolved in ethanol (10 ml), then hydrochloric acid (1 ml) and compound **2** (400 mg, 1.3 mmol) in 10 ml ethanol were added dropwise. The mixture was refluxed for 2 h (TLC monitoring). After cooling down to room temperature, the mixture was extracted with chloroform (3× 10 ml), dried over magnesium sulfate. After filtration, the solvent was evaporated to dryness under reduced pressure. Upon recrystallisation, the phenazine **6b** was obtained as yellow crystals, yield: 330 mg (84%). m.p. 159.7–161.2 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.56 (d, J = 8 Hz, 2H), 9.24 (t, J = 10 and 1.2 Hz, 2H), 8.10 (d, J = 9 Hz, 1H), 7.90 (d, J = 11.5 Hz, 1H), 7.78–7.75 (m, 2H), 3.87 (m, 1H), 3.76 (s, 3H), 3.49 (m, 1H), 2.52 (dd, J = 12.6 and 1.8 Hz, 1H), 2.47 (d, J = 11.3 Hz, 1H), 2.03–1.78 (m, 5H), 1.65 (m, 2H), 1.42 (s, 3H), 1.41 (s, 3H); ^{13}C NMR ($CDCl_3$ 125 MHz) δ: 179.0, 153.2, 152.9, 149.9, 140.1, 139.4, 136.2, 134.0, 132.7, 132.4, 130.1, 129.1, 129.0, 128.6, 127.0, 126.0, 121.6, 121.5, 52.0, 47.8, 45.1, 38.0, 37.9, 36.5, 29.7, 26.0, 24.7, 21.3, 18.6, 16.6; IR (KBr, cm^{-1}): 2936, 1724, 1635, 1361, 1248, 1114, 742; anal. calcd for $C_{30}H_{28}N_4O_2$, C, 75.61; H, 5.92; N, 11.76; found: C, 75.50; H, 5.91; N, 11.68; MS (FAB): 477 (M^++1).

2.3. Preparation of **7**

A mixture of **2** (302 mg, 1 mmol), acenaphthenequinone (200 mg, 1.1 mmol) and glacial acetic acid (10 ml) was heated under reflux and N_2 for 2 h. After removal of solvent, the crude product was re-crystallized with absolute methanol. Quinoxaline **7** was obtained as light yellow crystals, yield: 380 mg (85%). m.p. 195.3–197.4 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.44–8.40 (m, 2H), 8.12–8.10 (m, 2H), 8.03 (d, J = 8.9 Hz, 1H), 7.86–7.84 (m, 2H), 7.74 (d, J = 9.0 Hz, 1H), 3.83–3.89 (dd, J = 18.5 and 6.2 Hz, 1H), 3.74 (s, 3H), 3.47–3.45 (m, 1H), 2.48 (d, J = 12.6 Hz, 1H), 2.42 (d, J = 11.0 Hz, 1H), 2.01–1.82 (m, 4H), 1.74–1.70 (m, 2H), 1.66–1.63 (m, 1H), 1.39 (s, 6H); ^{13}C NMR ($CDCl_3$ 125 MHz) δ: 179.0, 152.2, 152.1, 150.7, 148.2, 141.4, 141.0, 140.0, 139.5, 133.5, 133.5, 133.4, 128.6, 128.0, 127.7, 127.0, 124.0, 52.1, 47.8, 45.2, 38.0, 37.8, 36.5, 26.0, 24.4, 21.3, 18.6, 16.5; anal. calcd for $C_{30}H_{28}N_2O_2$, C, 80.33; H, 6.29; N, 6.25; found: C, 80.15; H, 6.37; N, 6.18; MS (FAB): 449 (M^++1).

2.4. Preparation of ***8a*–*8b***

Methyl 12-bromo-13,14-diaminodeisopropyldehydroabietate **3** (380 mg, 1 mmol) was dissolved in 5 ml absolute ethyl alcohol. Then indole-2,3-dione (200 mg, 1.4 mmol) in 10 ml acetic acid was added dropwise. The mixture was stirred and refluxed for 2 h. The solvent was evaporated to dryness under reduced pressure. Two products, quinoxaline **8a** and **8b**, were separated by column chromatography on silica gel with light petroleum ether: acetic acid (10:3).

8a: yellow crystals, yield: 120 mg (24%). m.p.178.5–179.9 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.70 (brs, 1H), 8.44 (d, J = 7.6 Hz, 1H), 8.06 (s, 1H), 7.66 (t, J = 7.9 and 7.2 Hz, 1H), 7.58 (d, J = 7.9 Hz, 1H), 7.39 (t, J = 7.6 and 7.2 Hz, 1H), 3.84–3.80 (dd, J = 19.6 and 6.6 Hz, 1H), 3.74 (s, 3H), 3.41–3.39 (m, 1H), 2.45–2.42 (m, 2H), 2.19 (m, 2H), 1.90–1.88 (m, 5H), 1.69 (s, 3H), 1.39 (s, 3H); ^{13}C NMR ($CDCl_3$ 125 MHz) δ: 179.0, 149.8, 141.4, 137.8, 135.5, 129.2, 129.1, 127.7, 127.2, 124.4, 122.5, 122.4, 120.7, 116.5, 112.0, 52.1, 47.8, 45.2, 38.0, 37.7, 36.5, 26.0, 24.4, 21.4, 18.6, 16.5. IR (KBr, cm^{-1}): 3433, 2925, 1697, 1612, 1463, 1385, 1249, 1129, 1110, 744, 731; anal. calcd for $C_{26}H_{26}BrN_3O_2$, C, 63.42; H, 5.32; N, 8.53; found: C, 63.28; H, 5.30; N, 8.39; MS (FAB): 493 (M^++1).

8b: light yellow crystals, yield: 260 mg (58%). m.p. 176.4–178.5 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 9.72 (brs, 1H), 8.50–7.30 (m, 5H), 3.72 (s, 3H), 3.52–3.48 (dd, 1H, J = 18.5 and 6.2 Hz), 3.28–3.24 (m, 1H), 2.48–2.34 (m, 2H), 1.96–1.60 (m, 7H), 1.36–1.30 (s, 6H); ^{13}C NMR ($CDCl_3$ 125 MHz) δ: 179.1, 149.8, 141.5, 136.5, 135.6, 133.3, 130.1, 129.1, 125.7, 123.7, 122.4, 121.5, 120.7, 116.5, 112.0, 52.1, 47.8, 45.2, 38.0, 37.7, 36.5, 26.0, 24.4, 21.4, 18.6, 16.5. Anal. calcd for $C_{26}H_{26}BrN_3O_2$, C, 63.42; H, 5.32; N, 8.53; found: C, 63.30; H, 5.31; N, 8.40; MS (FAB): 493 (M^++1).

2.5. Preparation of ***9a*–*9b***

A mixture of **2** (150 mg, 0.5 mmol), 1,8-naphthalene dianhydride (100 mg, 0.5 mmol) and glacial acetic acid (20 ml) was heated under reflux and N_2 for 3 h. The mixture was evaporated to dryness and purified by column chromatography twice eluting with

petroleum ether:ethyl acetate (5:2) and benzene:chloroform (1:1), respectively. Two products were isolated: naphthalimides **9a** and **9b**.

9a: yellow soild, yield: 40 mg (17%). m.p. 187.1–189.3 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.80–8.79 (d, J = 7.2, 1H), 8.71–8.69 (d, J = 7.2, 1H), 8.27–8.25 (d, J = 8.1, 1H), 8.14–8.12 (d, J = 8.1, 1H), 7.83–7.78 (m, 2H), 7.70–7.68 (d, J = 8.5, 1H) (位), 7.52–7.50 (d, J = 8.5, 1H) (位), 3.75 (s, 3H), 3.75 (m, 1H), 3.44–3.40 (m, 1H), 2.45–2.43 (m, 2H), 2.01–1.82 (m, 4H), 1.74–1.70 (m, 2H), 1.66–1.63 (m, 1H), 1.30 (s, 3H), 1.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.0, 160.7, 150.6, 148.0, 142.7, 134.4, 131.9, 131.3, 130.9, 127.4, 126.9, 124.0, 127.0, 127.0, 125.1, 124.5, 121.6, 117.7, 52.1, 47.7, 44.9, 39.2, 38.6, 36.4, 30.6, 29.7, 25.4, 21.6, 18.8, 16.7; anal. calcd for $C_{30}H_{28}N_2O_3$, C, 77.56; H, 6.08; N, 6.05; found: C, 77.45; H, 6.07; N, 5.92; MS (FAB): 465 (M^++1).

9b: light yellow crystals, yield: 130 mg (56%). m.p. 190.3–193.1 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ: 8.76–8.74 (d, J = 7.3, 1H), 8.70–8.69 (d, J = 7.3, 1H), 8.26–8.24 (d, J = 8.5, 1H), 8.21–8.19 (d, J = 8.1, 1H), 8.04–8.03 (d, J = 8.1, 1H), 7.75 (m, 1H), 7.71 (m, 1H), 7.40–7.38 (d, J = 8.6, 1H), 3.73 (s, 3H), 3.49–3.45 (m, 1H), 3.27–3.25 (m, 1H), 2.45–2.43 (m, 2H), 2.01–1.82 (m, 4H), 1.74–1.70 (m, 2H), 1.66–1.63 (m, 1H), 1.33 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 179.0, 160.6, 148.4, 146.9, 142.5, 135.0, 132.2, 131.3, 130.8, 129.1, 128.8, 127.1, 126.8, 123.3, 121.8, 120.9, 113.1, 51.9, 47.8, 45.2, 38.5, 37.6, 36.7, 29.7, 28.9, 25.5, 25.2, 18.7, 16.6; anal. calcd for $C_{30}H_{28}N_2O_3$, C, 77.56; H, 6.08; N, 6.05; found: C, 77.46; H, 6.07; N, 5.92; MS (FAB): 465 (M^++1).

2.6. Preparation of ***10a–10d***

2.6.1. General procedure

Methyl 12-bromo-13-nitro-7-oxo-dehydrodeisopropylabietate **4** (1 mmol) was added to the mixture of arylboronic acid (1.5 mmol), $Pd(OAc)_2$ (3 mol%) and K_2CO_3 (3 equiv.) in DMF (5 ml) and water (1 ml). The reaction mixture was stirred at 150 °C for 24 h. When cooled, water (20 ml) was added to the reaction mixture, extracted with ethyl acetate (3× 10 ml), dried over magnesium sulfate. After filtration, the solvent was evaporated to dryness under reduced pressure, and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate 5:2).

2.6.2. ***10a***

Red solid, yield: 28%. m.p. 206.3–207.6 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.80 (d, J = 7.05 Hz, 1H), 7.75 (d, J = 7.4 Hz, 1H), 7.44 (m, 1H), 7.38 (m, 2H), 7.33 (s, 1H), 6.89 (s, 1H), 3.89 (s, 2H), 3.69 (s, 3H), 2.76 (m, 2H), 2.36 (m, 2H), 1.88–1.71 (m, 5H), 1.37 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.7, 177.9, 147.5, 146.7, 138.9, 133.7, 133.3, 133.3, 130.6, 127.8, 127.8, 126.3, 113.0, 112.9, 52.1, 46.8, 44.4, 37.7, 37.3, 36.7, 23.8, 23.8, 18.4; anal. calcd for $C_{24}H_{27}NO_2$, C, 73.36; H, 7.21; N, 3.71; found: C, 73.21; H, 7.18; N, 3.63; positive APCIMS m/z (relative intensity) 378.2 [M+H] + (100).

2.6.3. ***10b***

Yellow rhomboid crystals, yield: 70%. m.p. 217.1–218.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.73 (m, 2H), 7.67 (m, 2H), 7.57 (m, 2H), 7.50 (m, 2H), 7.41 (t, J = 6.5 Hz, 2H), 7.19 (s, 1H), 3.69 (s, 3H), 3.87 (s, 2H), 2.76 (m, 2H), 2.36 (m, 2H), 1.92–1.64 (m, 5H), 1.37 (s, 3H), 1.31 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.2, 177.9, 146.1, 142.0, 140.8, 140.5, 137.8, 133.2, 130.9, 129.2, 129.2, 128.9, 128.9, 127.7, 127.7, 127.6, 127.1, 127.1, 125.7, 113.2, 52.2, 46.7, 44.1, 37.9, 37.4, 36.9, 36.6, 23.9, 18.2, 16.4; IR (KBr, cm^{-1}): 3445, 3378, 3028, 2864, 2845, 1723, 1678, 1619, 1484, 1421, 1344, 1312, 1243, 1113, 1066, 1007, 848, 769, 735, 698, 621, 571; anal. calcd for $C_{30}H_{31}NO_3$, C, 77.44; H, 6.89; N, 3.09; found: C, 77.21; H, 6.88; N, 3.01; EIMS 70 eV m/z (relative intensity): 453 [M] + (54), 427 (1), 394 (2), 378 (100), 352 (5), 189 (8), 169 (4).

2.6.4. ***10c***

Red solid, yield: 79%. m.p. 243.9–245.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.95 (t, J = 6.9 Hz, 2H), 7.62–7.53 (m, 3H), 7.50–7.44 (m, 3H), 7.19 (d, J = 2.9 Hz, 1H), 3.71 (s, 3H), 3.56 (s, 2H), 2.80 (m, 2H), 2.39 (m, 1H), 2.25 (d, J = 11.7 Hz, 1H), 1.88–1.62 (m, 5H), 1.37 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.4, 178.0, 145.7, 142.9, 136.3, 133.8, 132.2, 131.2, 128.5, 128.4, 127.2, 127.1, 126.5, 126.2, 125.7, 125.7, 125.6, 112.8, 52.2, 46.8, 44.2, 37.9, 37.3, 36.9, 36.6, 23.4, 18.2, 16.4. IR (KBr, cm^{-1}): 3473, 3377, 2996, 2949, 2924, 2865, 1714, 1676, 1619, 1493, 1415, 1344, 1310, 1257, 1240, 1115, 1083, 814, 793, 783, 668, 572; anal. calcd for $C_{28}H_{29}NO_3$, C, 78.66; H, 6.84; N, 3.28; found: C, 78.60; H, 6.82; N, 3.16; EIMS 70 eV m/z (relative intensity): 427 [M] + (56), 412 (1), 368 (2), 352 (100), 298 (5), 176 (3), 156 (4).

2.6.5. ***10d***

Red rhomboid crystals, yield: 75%. m.p. 209.7–210.3 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.97 (s, 1H), 7.95 (d, J = 4.0 Hz, 1H), 7.91 (dd, J = 9.3 and 4.7 Hz, 1H), 7.60 (dd, J = 8.4 and 1.7 Hz, 1H), 7.55 (m, 2H), 7.43 (s, 1H), 7.23 (s, 1H), 3.69 (s, 3H), 3.88 (s, 2H), 2.77 (m, 2H), 2.37 (m, 2H), 1.89–1.67 (m, 5H), 1.37 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 198.3, 177.9, 146.1, 142.2, 136.3, 133.5, 132.7, 130.9, 128.7, 128.5, 128.1, 127.8, 127.7, 126.7, 126.6, 126.5, 125.9, 113.2, 52.2, 46.7, 44.1, 37.9, 37.3, 36.9, 36.6, 23.9, 18.1, 16.4. IR (KBr, cm^{-1}): 3482, 3386, 2977, 2949, 2923, 2884, 1710, 1674, 1616, 1495, 1412, 1267, 1235, 1115, 1064, 966, 899, 866, 825, 757, 644, 620, 572; anal. calcd for $C_{28}H_{29}NO_3$, C, 78.66; H, 6.84; N, 3.28; found: C, 78.60; H, 6.82; N, 3.16; EIMS 70 eV m/z (relative intensity): 427 [M] + (58), 412 (1), 368 (2), 352 (100), 298 (6), 286 (3), 176 (4), 156 (5).

2.7. Preparation of ***11a–11b***

230 mg KF–Al_2O_3 (1.4 mmol) was added to a solution of 360 mg **5** (1 mmol) in 15 ml methanol. After 10 min, 160 mg 1-naphthaldehyde (1 mmol) dissolved in 1 ml CH_2Cl_2 were added, and the mixture was stirred and refluxed for 7 h. After filtration, the solvent was evaporated to dryness under reduced pressure. The residue was purified by TLC eluting with carbon tetrachloride: methylene chloride (1:1); compound **11a** was obtained as a yellow oil. Yield: 350 mg (71.5%). m.p. 160.9–161.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.22 (d, J = 16.1, 1H), 8.02 (d, J = 6.7, 1H), 7.86 (d, J = 8.2, 1H), 7.82 (d, J = 6.8, 1H), 7.77 (d, J = 7.3, 1H), 7.49–7.44 (m, 3H), 7.29 (d, J = 4.6, 1H), 7.09 (d, J = 16.1, 1H), 7.04 (s, 1H), 3.63 (s, 3H), 3.25 (m, 1H), 2.65 (m, 2H), 2.24 (m, 2H), 1.86–1.54 (m, 5H), 1.40–1.42 (m, 2H), 1.23 (s, 3H), 1.20 (s, 3H), 1.18 and 1.21 (d, J = 6.8, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.6, 178.9, 146.6, 144.7, 142.5, 137.9, 136.6, 133.8, 132.1, 131.6, 130.7, 128.8, 128.6, 126.9, 125.5, 125.1, 124.0, 123.3, 52.0, 47.7, 45.0, 38.1, 37.1, 36.7, 30.2, 29.3, 25.1, 24.3, 24.1, 21.5, 18.5, 16.5; IR (KBr, cm^{-1}): 3066, 2929, 1714, 1449, 1360, 1246, 1113, 1034, 758, 724; anal. calcd for $C_{34}H_{38}O_3$, C, 82.55; H, 7.24; found: C, 82.50; H, 7.23; positive APCIMS m/z (relative intensity) 495 [M+H] + (100).

11b was obtained by following a procedure similar to that used for **11a** using 9-anthraldehyde instead of 1-naphthaldehyde. Compound **11b** was obtained as a yellow solid. Yield: 470 mg (84.7%). m.p. 172.9–174.1 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.31 (s, 1H), 8.17 (d, J = 8.6, 2H), 7.93 (d, J = 8.1, 2H), 7.82 (s, 1H), 7.80 (d, J = 12.6, 1H), 7.49–7.42 (m, 4H), 7.14 (d, J = 12.6, 1H), 6.63 (s, 1H), 3.67 (s, 3H), 3.10 (m, 1H), 2.66 (m, 2H), 2.23 (dd, J = 2.2 and 12.4, 1H), 2.03 (d, J = 12.7, 1H), 1.88 (m, 1H), 1.66–1.62 (m, 4H), 1.59 (m, 2H), 1.31 (s, 3H), 1.28 and 1.23 (d, J = 6.9, 6H), 1.20 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 197.1, 178.9, 146.7, 144.9, 142.8, 138.2, 136.7, 136.3, 134.1, 131.4,

129.7, 129.5, 128.9, 128.7, 127.2, 126.9, 126.4, 125.8, 125.4, 125.2, 124.1, 124.0, 51.9, 47.6, 44.8, 38.1, 37.1, 36.6, 30.0, 29.4, 25.1, 24.3, 24.1, 21.5, 18.5, 16.5; anal. calcd for $C_{38}H_{40}O_3$, C, 83.79; H, 7.40; found: C, 83.70; H, 6.38; IR (KBr, cm^{-1}): 3066, 2929, 1714, 1449, 1360, 1246, 1113, 1034, 758, 724; positive APCIMS *m*/*z* (relative intensity) 545 [M+H]+(100).

3. Results and discussion

3.1. Synthesis and characterization

Phenazine **6a** was prepared in good yields (82.9%) by mild acid catalyzed condensation of methyl 13,14-diaminodeisopropyldehydroabietate **2** with phenanthrenequinone. It should be note that when using concentrated hydrochloric acid instead of glacial acetic acid, the yield of **6a** was reduced to 35%. However, strong acidic condition promotes the condensation of **2** with 1,10-phenanthroline-5,6-dione, the reaction in the solvent of ethanol and hydrochloric acid afforded phenazine **6b** in 84% yield. Quinoxaline **7** was obtained by simple cyclo-condensation of **2** with acenaphthenequinone in glacial acetic acid. The condensation of **3** with indole-2,3-dione in a mixture of glacial acetic acid and ethanol gave two stereomeric quinoxalines **8a** (yield 24%) and **8b** (yield 58%), which were separated by chromatography (petroleum ether/ethyl acetate 10:3). Naphthalimides **9a** (yield 17%) and **9b** (yield 56%) were also obtained as stereoisomers, separated by chromatography (benzene/chloroform 1:1). The structural assignments of compounds **6a**–**9b** were based on NMR, IR and MS spectral data, which were fully consistent with the proposed structures. The ^1H and ^{13}C spectra of the diterpenic part of molecules of **6a**–**9b** have many similarities with those of compound **2** and **3** [**2d**], and therefore most protons and carbons could be immediately assigned. The structure of **8a** and **8b**, **9a** and **9b** were elucidated based on the analysis of ^1H NMR. The resonance of indole NH was assigned as a broad one-proton singlet at δ 9.70 and 9.72 ppm for **8a** and **8b**, respectively. In compound **8a**, 7-CH_2 protons resonances appear at 3.40 and 3.82 ppm, downfield shifted from the corresponding resonances of the compound **8b** (3.25 and 3.50 ppm), due to the effect of indole nitrogen. In **9a**, 7-CH_2 protons resonances appear as multiplets at 3.44 and 3.75 ppm, H-12 resonance appears as a doublet at 7.50 ppm, and in **9b** the corresponding resonances appear at 3.25, 3.48 and 8.25 ppm. This different chemical shifts between **9a** and **9b** are caused by the deshielding effect of 18-carbonyl.

Compounds **10a**–**10d** were synthesized by palladium-catalyzed Suzuki cross-coupling reaction with arylboronic acids at 150 °C in a mixture of DMF and H_2O (5/1) in the presence of $Pd(OAc)_2$ and K_2CO_3 (Scheme 2). In this reaction, Suzuki cross-coupling reaction and nitro reduction reaction synchronously occurred without affecting the other reducible ester and carbonyl groups [15]. All the four compounds gave IR spectra with typical absorption for arylamino groups between 3500 and 3300 cm^{-1}. The IR bands at about 1710 and 1670 cm^{-1} can be assigned to the C=O($COOCH_3$) and the C=O (ketone) stretching mode, respectively. The NMR signal due to 13-amino protons appeared as singlets at δ 3.89 in **10a**, δ 3.87 in **10b**, δ 3.56 in **10c** and δ 3.88 in **10d**. The carbonyl resonance was fond at about 198 ($COOCH_3$) and 178 (ketone) ppm. Next, the signal of 14-H is distinguishedly observed in a lower magnetic field than those of the other protons by the effect of 7-oxo group and 13-amino group. The mass spectra all give corresponding molecular ion peaks, respectively.

Compounds **11a**–**11b** were obtained with good yields by base (KF–Al_2O_3) catalyzed Aldol condensation of methyl 12-acetyldehydroabetate **5** with 9-anthraldehyde and 1-naphthaldehyde in methanol (Scheme 2). The assigned of the

Table 1
The absorption and fluorescence spectral properties of compounds **6a**–**11b** in methanol solution.

Compounds	$\lambda_{abs,max}$ (nm)[a]	ε[b] ($\times 10^{-4}$ M^{-1} cm^{-1})	$\lambda_{em,max}$ (nm)[a]	Φ_f
6a	255	3.31	430	0.0153
6b	251	7.83	471	0.0109
7	280	9.67	448	0.0152
8a	278	6.47	489	0.0153
9a	242	8.82	515	0.0517
9b	230	5.86	514	0.0325
10b	208	7.63	470	0.0172
10c	220	6.83	465	0.0156
10d	221	7.82	465	0.0182
11a	250	6.62	404	0.0013
11b	255	7.41	416	0.0018
1	220	–	300	-

[a] Absorption (1.0×10^{-5} mol/l) and fluorescence (1.0×10^{-5} mol/l) spectra at room temperature in methanol solution.
[b] Referenced to the molar extinction coefficient of the peak with the strongest absorption.

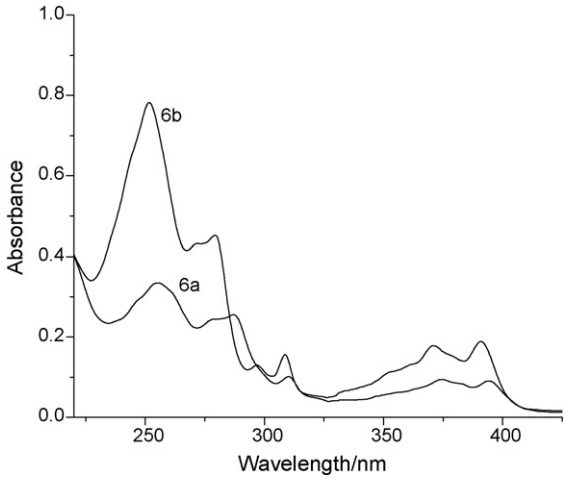


Fig. 2. UV–vis absorption spectra of the compounds **6a** and **6b** in methanol (concentration: 1.0×10^{-5} mol/l).

^1H NMR and ^{13}C NMR resonances of **11a** and **11b** were made taking into account the spectra of their precursor **5** [16]. The NMR data for compound **11a**, similar to compound **11b**, show that methyl groups 16 and 17 are no longer equivalent, appearing with distinct ^1H (δ = 1.18 and 1.21 ppm) and ^{13}C (δ = 24.1 and 24.3 ppm)

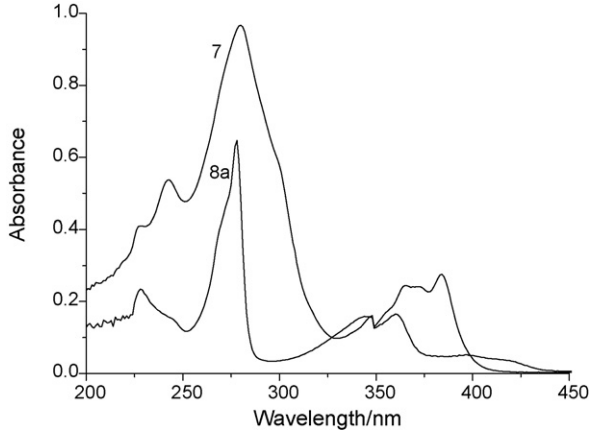


Fig. 3. UV–vis absorption spectra of the compounds **7** and **8a** in methanol (concentration: 1.0×10^{-5} mol/l).

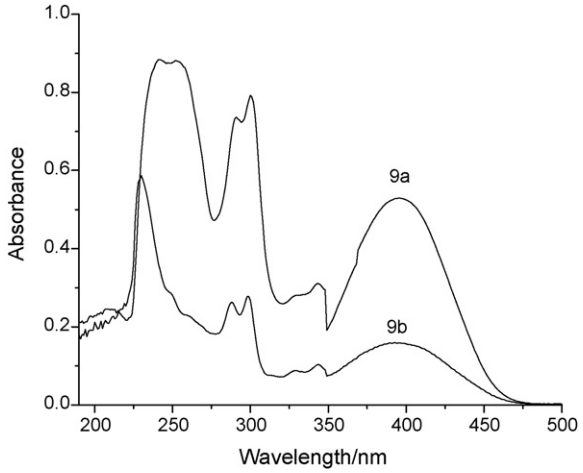


Fig. 4. UV–vis absorption spectra of the compounds **9a** and **9b** in methanol (concentration: 1.0×10^{-5} mol/l).

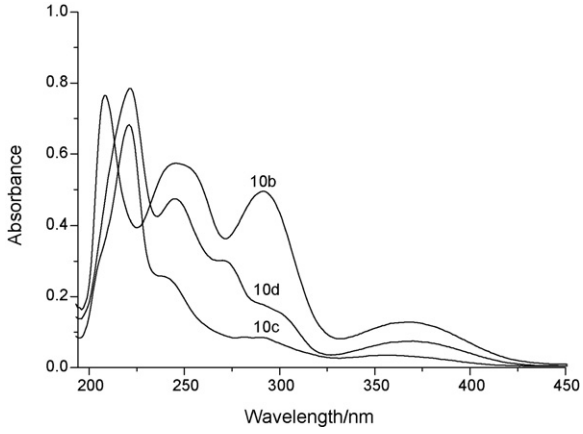


Fig. 5. UV–vis absorption spectra of the compounds **10b**–**10d** in methanol (concentration: 1.0×10^{-5} mol/l).

resonances. The olefinic protons (CH=CH) resonances appear as doublets (J = 16.1 Hz) at 8.22 and 7.09 ppm, respectively, indicating a *trans* stereochemistry of this double bond. Their structures were consistent with their IR spectra (**11a**: ν 1721, 1670 cm^{-1} and **11b**: ν 1723, 1671 cm^{-1}).

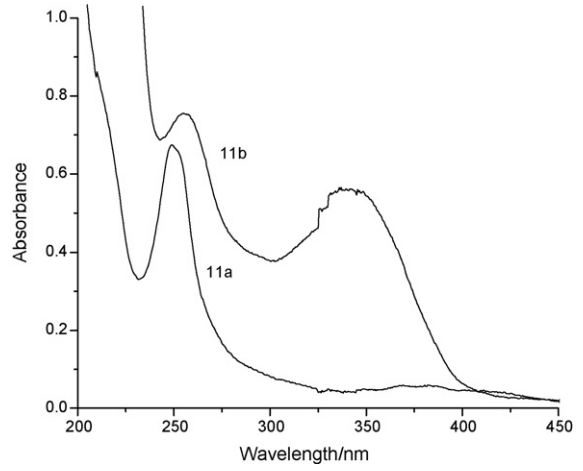


Fig. 6. UV–vis absorption spectra of the compounds **11a** and **11b** in methanol (concentration: 1.0×10^{-5} mol/l).

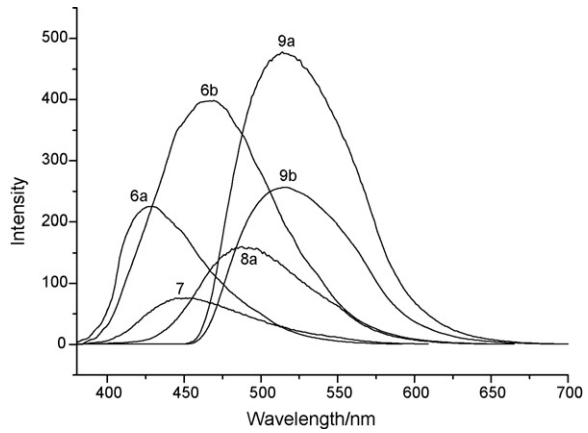


Fig. 7. Fluorescence emission spectra of the compounds **6a**, **6b**, **7**, **8a**, **9a** and **9b** in methanol (concentration: 1.0×10^{-5} mol/l).

3.2. UV–vis and fluorescence spectra

The UV–vis and fluorescence spectra of compounds **6a**–**11b** were measured in methanol solution at a concentration of 1.0×10^{-5} mol/l and the results were listed in Table 1, which also contains the data of the dehydroabietic acid **1** for comparison. It could be seen that these investigated compounds present an absorption maximum in the UV region at $\lambda_{max}^{abs} = 208 - 280$ nm with molar extinction coefficients ε values ($10^4\ M^{-1}\ cm^{-1}$) in agreement with π–π^* transitions. These investigated compounds exhibit the fluorescence emission maxima ranging from 404 to 515 nm (Figs. 7 and 8), displaying a marked red-shift of 104–215 nm on the fluorescence emission maxima compared with dehydroabietic acid **1**. The fluorescence quantum yield was determined from the absorption and fluorescence spectra of compounds **6a**–**11b** in methanol at a concentration of 1.0×10^{-5} mol/l. In most cases, the fluorescence quantum yields are found in the range between 0.01 and 0.02 (Table 1). Somewhat larger values are found for naphthalimide **9b** (0.0325), and **9a** (0.0517).

The absorption spectra of **6a** and **6b** are presented in Fig. 2 and show the absorption maximum at 255 and 251 nm, respectively. A very small blue-shift (~4 nm) on the absorption maximum could be detected (from **6a** to **6b**). Compared to the emission spectra of compound **6a** in methanol, a 41 nm red-shift of the emission maximum of **6b** was observed. Fig. 3 shows UV–vis absorption of two quinoxalines **7** and **8a** in methanol solution. The absorption peaks of two compounds appeared at around 280 and 278 nm, respectively. Quinoxaline **8a** exhibits bright green emission with peak at 489 nm. Fig. 4 compares the absorption spectra of naphthalimides **9a** and **9b** in methanol. It is shown that the absorption spectrum of naphthalimides **9a** and **9b** showed broad π–π^* transition band around 395 nm, the two compounds display bright and intensive yellow-green fluorescence with peak at about 515 nm.

The absorption and fluorescence spectra of compounds **10b**–**10d** are similar in shape. As shown in Figs. 5 and 8, the three compounds present an absorption maximum (λ_{max}^{abs}) in the 208–220 nm region, having a blue fluorescence with the maximum at around 470 nm. The UV–vis absorption spectra of **11a** and **11b** in methanol are presented in Fig. 6. Clearly, **11b** exhibits two typical π–π^* absorption bands centered at λ = 255 nm ($\varepsilon = 7.41 \times 10^4\ M^{-1}\ cm^{-1}$) and 336 nm ($\varepsilon = 5.55 \times 10^4\ M^{-1}\ cm^{-1}$), respectively. As the conjugation length of **11b** is longer than that of **11a**, bathochromic and hyperchromic shifts were observed. In the fluorescence emission spectra (Fig. 8), three fluorescence emission peaks can be seen in the **11b**, whereas **11a** showed very weak fluorescence signal with one emission peak at 404 nm. In comparison with the emission spectra of compound **11b**, **10b** shows a remark-

Table 2
Fluorescence emission maxima (nm) of compounds **6a–11b** in solvents of different polarity.

Compound	Methanol	Dioxane	THF	Dichloromethane	Cyclohexane
6a	430	449	459	432	452
6b	471	462	459	450	431
7	448	449	451	452	460
8a	489	460	467	454	449
9a	515	505	509	480	465
10b	470	468	470	457	449
10c	465	475	467	449	442
10d	465	462	468	452	443
11a	404	385	381	378	368
11b	416	390	388	363	360

able red-shift and an increase of fluorescence intensity, though the conjugation length of **11b** is longer than that of **10b**, which is mainly attributed to the electron donor character of 13-amino group.

The fluorescence emission maxima of compounds **6a–11b** in methanol, THF, dioxane, dichloromethane and cyclohexane are presented in Table 2. It is shown that an increase of the solvent polarity (from cyclohexane to methanol) promotes a significant red-shift of the emission spectra, but blue-shift in the case of compound **7**. Figs. 9 and 10 illustrate the changes in the fluorescence band for compounds **7** and **8a** in solvents of different polarity, respectively.

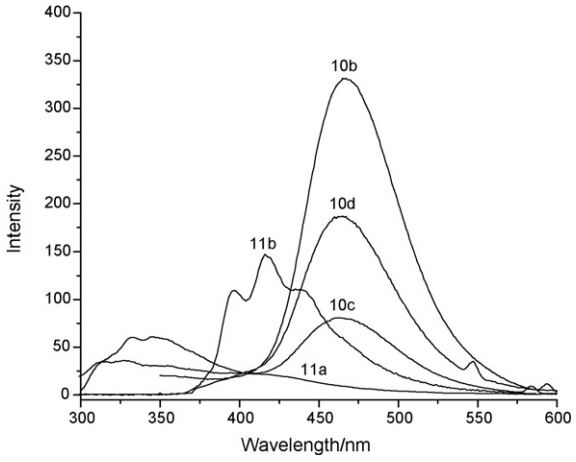


Fig. 8. Fluorescence emission spectra of the compounds **10b**, **10c**, **10d**, **11a** and **11b** in methanol (concentration: 1.0×10^{-5} mol/l).

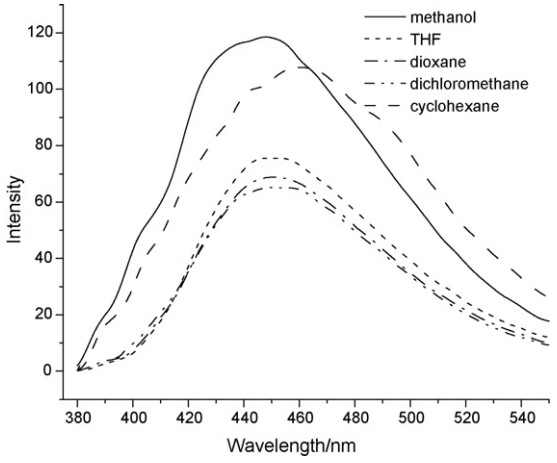


Fig. 9. Fluorescence emission spectra of the compound **7** in solvents of different polarity (concentration: 1.0×10^{-5} mol/l).

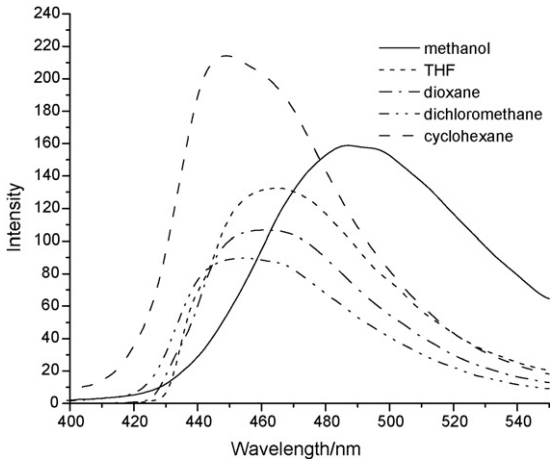


Fig. 10. Fluorescence emission spectra of the compound **8a** in solvents of different polarity (concentration: 1.0×10^{-5} mol/l).

4. Conclusions

The aim of this work was the syntheses and the investigation of fluorescence characteristics of two series of dehydroabietic acid C-ring derivatives.

The structure of the prepared compounds was confirmed by elemental analysis, MS, NMR and IR spectra.

The UV–vis absorption and fluorescence spectra and fluorescence quantum yields were measured in methanol solution. It has been found that the absorption maximum are in the UV region at $\lambda_{max}^{abs} = 208–280$ nm and the fluorescence maxima are in the spectral range 404–515 nm. The results showed that both absorption and emission maxima wavelengths of the compounds exhibit a marked bathochromic shift with respect to dehydroabietic acid **1** due to the multiple aromatic rings with rigid planar structures or the larger conjugation of benzene moiety.

Acknowledgments

We are grateful for financial support from the National Natural Science Foundation of China (30460153), and the open fund of Key Laboratory of Development & Application of Forest Chemicals of Guangxi (GXFC08-05), and the Project of Ten, Hundred, Thousand Distinguished Talents in New Century of Guangxi (No. 2007228).

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