



# Chemical constituents of the Vietnamese plants *Dalbergia tonkinensis* Prain and *Cratoxylum formosum* (Jack) Dyer in Hook and their DPPH radical scavenging activities

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## Abstract

Phytochemical investigations of the leaves and roots of *Dalbergia tonkinensis* led to the isolation of a new isoflavone glycoside derivative, isocaviunin 7-*O*- $\beta$ -D-apiofuranosyl-(1  $\rightarrow$  6)- $\beta$ -D-glucopyranoside (**1**), and a new scalemic sesquiterpene lactone, 3,7-dimethyl-3-vinylhexahydro-6,7-bifuran-3(2*H*)-one (**2**), along with the previously known compounds **3-16**, and nine other known compounds **17-25** were isolated from the leaves of *Cratoxylum formosum*. The chemical structures of the isolated compounds were elucidated by 1D- and 2D-NMR analyses as well as MS spectroscopic data. The results suggest that flavonoids are characteristic of both plants. In the DPPH radical scavenging assay, (3*R*)-vestitol (**5**) and isoquercetin (**24**) possessed the strongest antioxidative IC<sub>50</sub> values of 42.20  $\mu$ g/mL and 45.63  $\mu$ g/mL, respectively, and their values were comparable to that of the positive control catechin (IC<sub>50</sub> 42.98  $\mu$ g/mL).

**Keywords** *Dalbergia tonkinensis* · *Cratoxylum formosum* · leaves · roots · DPPH radical scavenging activity

## Introduction

The rare plant *D. tonkinensis*, locally called “Sua do”, is an endemic and perennial species native to Vietnam. In terms of its conservation status, this plant is classified as vulnerable on the Red List of Threatened Species of the International Union for Conservation of Nature and Natural Resources (IUCN); thus, its exploitation, shipping and storage is prohibited (Cuong et al. 2017; Son et al. 2017, 2018a, 2018b). The preliminary screenings suggested that this species possessed a wide spectrum of biological activities such as anti-bacterial activity and alpha-glucoside

inhibition (Nguyen et al. 2018), but to date, the phytochemical studies on this plant have been quite limited. On the other hand, *Cratoxylum formosum* (Jack) Dyer in Hook (other names include Mampat or *Cratoxylum formosum* subsp. *formosum* species) belongs to the family Clusiaceae (Guttiferae) and is widely distributed in countries in southeastern Asia; the plant *C. formosum* subsp. *pruniflorum* (Kurz) Gogelein is a subspecies of *Cratoxylum formosum* (Jack) Dyer in Hook (Gogelein 1967). To the best of our knowledge, there has been only one report on its phytochemical constituents, as well as on its intracellular antioxidant and anti-inflammatory activities until now (Choi et al. 2012).

In this paper, we report the isolation and structural elucidation of new compounds **1-2** as well as the DPPH radical scavenging activities of the isolated compounds.

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## Experimental

### General experimental procedures

<sup>1</sup>H-NMR (500 MHz) and <sup>13</sup>C-NMR (125 MHz) were measured using a Bruker 500 MHz. HR-FAB-MS/FAB-MS were obtained from a JEOL MStation JMS-700. IR, UV,

and optical rotation spectra were recorded by a JASCO FT-IR 410 infrared spectrophotometer, JASCO V-650 spectrophotometer, and JASCO P-2300 polarimeter, respectively. Column chromatography was carried out on silica gel (Si 60 F<sub>254</sub>, 40–63 mesh, Merck). Precoated TLC plates (Si60 F<sub>254</sub>) were used for analytical purposes. The compounds were visualized under UV radiation (254 and 365 nm) and by spraying plates with 10% H<sub>2</sub>SO<sub>4</sub> followed by heating with a heat gun.

### Plant material

The whole plant of *D. tonkinensis* was collected in Quangbinh Province, Vietnam in 2016. The leaves of *C. formosum* were collected in Ninhbinh Province, Vietnam in 2010. These plants were identified by Dr. Nguyen Quoc Binh, Vietnam National Museum of Nature, Hanoi, Vietnam. The voucher specimens (C-575 for *D. tonkinensis* and C-437 for *C. formosum*) have been deposited at the Department of Bioactive Products, Institute of Natural Products Chemistry, VAST, Hanoi, Vietnam.

### Extraction and isolation

The leaves (2.0 kg) of *D. tonkinensis* were extracted with MeOH (10.0 L) for 4 h using a Soxhlet extractor to produce the MeOH crude extract (300.0 g). This extract was then suspended in hot MeOH–H<sub>2</sub>O (1:1, v/v) and successively partitioned with CHCl<sub>3</sub> and EtOAc to yield the corresponding fractions (frs.). The H<sub>2</sub>O-soluble residue (fr. W, 95.5 g) underwent chromatography on a Diaion HP-20 column [H<sub>2</sub>O–MeOH (1:0, 1:3, 0:1, v/v)], to afford 3 frs. W1–W3. The fr. W2 (4.57 g) was separated by silica gel column chromatography [CHCl<sub>3</sub>–MeOH–H<sub>2</sub>O (3:1:0.1, v/v/v)] to yield compound **14** (20.6 mg) and nine frs. W21–W29. Then, fr. W27 (0.9 g) was purified by HPLC [Cosmosil 5C18-AR-II column (10 × 250 mm) with MeOH–H<sub>2</sub>O (7:3, v/v, 1 mLmin<sup>-1</sup>), UV 210 nm] to give compound **1** (1.2 mg), and compound **12** (4.6 mg) was obtained from fr. W28 (1.9 g) in the same manner. Utilizing HPLC [Cosmosil 5C18-AR-II column (10 × 250 mm), MeOH–H<sub>2</sub>O–HCOOH (3:1:0.1%, 2 mLmin<sup>-1</sup>), UV 254 nm], compound **13** (1.6 mg) was obtained from fr. W29 (0.6 g). Using column chromatography over silica gel [CHCl<sub>3</sub>–MeOH (99:1, v/v)], the CHCl<sub>3</sub> fr. (60.7 g) was separated to give eight frs. (C1–C8). Compound **8** (15.6 mg) was isolated from fr. C6 (5.7 g) by silica gel column chromatography [CHCl<sub>3</sub>–MeOH (3:1, v/v)].

The dried powdered roots (2.0 kg) were mixed with EtOH (10.0 L) for 4 h in a Soxhlet extractor, affording the crude EtOH extract (200.0 g). This crude extract was resuspended in hot MeOH–H<sub>2</sub>O (1:1, v/v) and partitioned with CH<sub>2</sub>Cl<sub>2</sub> and EtOAc to yield the corresponding fractions.

The root CH<sub>2</sub>Cl<sub>2</sub> fr. (45.5 g) underwent chromatography on a normal silica gel column [CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>COCH<sub>3</sub> (3:1, v/v)] to afford 6 frs. D1–D6. Compounds **3** (15.0 mg) and **4** (5.5 mg) were separated from fr. D1 (2.1 g) by silica gel column chromatography [*n*-hexane–CH<sub>3</sub>COCH<sub>3</sub> (3:1, v/v)]. The fr. D2 (3.2 g) then underwent chromatography on a Sephadex LH-20 column [MeOH–H<sub>2</sub>O (1:1, v/v)] to yield compounds **5** (3.1 mg), **9** (4.2 mg), **10** (2.1 mg) and **11** (3.99 mg). Compounds **2** (1.1 mg), **15** (2.0 mg) and **16** (2.5 mg) were purified from fr. D3 (2.7 g) by silica gel column chromatography [CHCl<sub>3</sub>–MeOH (3:1, v/v)] and HPLC [Cosmosil 5C18-AR-II column (10 × 250 mm), MeOH–H<sub>2</sub>O–HCOOH (3:1:0.1%, 2 mLmin<sup>-1</sup>), UV 254 nm]. The EtOAc root fr. (30.5 g) was purified on a normal silica gel column [CHCl<sub>3</sub>–MeOH–H<sub>2</sub>O (3:1:0.1, v/v/v)] to afford frs. E1–E7. Then, fr. E2 (0.85 g) was purified by HPLC [Cosmosil 5C18-AR-II column (10 × 250 mm), MeOH–H<sub>2</sub>O (7:3, 2 mLmin<sup>-1</sup>), UV 210 nm] to give compounds **6** (0.7 mg) and **7** (1.3 mg).

Dried leaves (2.0 kg) of *C. formosum* were extracted with MeOH (10.0 L, 3 times) at room temperature to produce the MeOH crude extract (220.0 g). This extract was then subjected to silica gel column chromatography and eluted with *n*-hexane, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>–EtOAc (8:2, v/v), CH<sub>2</sub>Cl<sub>2</sub>–EtOAc (1:1, v/v), EtOAc, EtOAc–MeOH (8:2, v/v) and EtOAc–MeOH (1:1, v/v), yielding the corresponding frs. Fr1–Fr7. Compounds **17** (45 mg) and **18** (15 mg) were obtained from fr. Fr1 (30.5 g) as white needles by silica gel column chromatography with *n*-hexane–CH<sub>3</sub>COCH<sub>3</sub> (3:1, v/v). Using silica gel column chromatography [CHCl<sub>3</sub>–MeOH (8:1, v/v)], fr. Fr4 (16.7 g) was separated to give four frs. Fr41–Fr44. Utilizing Sephadex LH-20 column chromatography with MeOH–H<sub>2</sub>O (1:1, v/v), compound **19** (37.5 mg) was obtained from fr. Fr42 (2.1 g). Meanwhile, compound **20** (200 mg) was precipitated out of fr. Fr44 (2.3 g) by silica gel column chromatography [CH<sub>2</sub>Cl<sub>2</sub>–MeOH–H<sub>2</sub>O (3:1:0.1, v/v/v)]. Similarly, the fr. Fr6 (20.5 g) was subjected to Sephadex LH-20 column chromatography with MeOH–H<sub>2</sub>O (2:1, v/v) to afford compound **21** (15.0 mg) and fr. Fr61. Then, fr. Fr61 (150 mg) was further subjected to HPLC [Cosmosil 5C18-AR-II column (10 × 250 mm), MeOH–H<sub>2</sub>O (7:3, v/v, 1.0 mL/min), UV 210 nm], to yield compounds **22** (5.4 mg), **23** (4.2 mg) and **24** (3.2 mg). Compound **25** (240 mg) was crystallized from the fr. Fr7 (30.1 g) in MeOH.

Isocaviunin-7-*O*-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside (**1**): White amorphous powder; [α]<sub>D</sub><sup>25</sup> = –266.9 (c 0.24, EtOH); IR (film): 3510, 3378, 2903, 1654, 1617, 1581, 1525, 1506, 1467, 1371, 1282, 1211, 1148, 1065, 980, 905, 853, 783, 678 cm<sup>-1</sup>; UV (EtOH) λ<sub>max</sub> nm (log ε): 295 (3.61), 263 (3.87), 205 (3.96); HR-FAB-MS: *m/z* 707.1577 [M + K]<sup>+</sup> (100%) (calcd. for C<sub>30</sub>H<sub>36</sub>O<sub>17</sub>K 707.1576), FAB-MS: *m/z* 707 [M + K]<sup>+</sup>, 669 [M + H]<sup>+</sup>,

**Table 1**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR data of compound **1**

Isocaviunin -7-O- $\beta$ -D-apiofuranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside ( <b>1</b> )					
Position	$\delta_{\text{H}}$ ( $J$ in Hz)	$\delta_{\text{C}}$	Position	$\delta_{\text{H}}$ ( $J$ in Hz)	$\delta_{\text{C}}$
2	8.24 (s)	155.7	2''	4.34 (m)	74.5
3		120.6	3''	4.78, (m)	77.7
4		181.2	4''	4.11 (m)	71.2
4a		106.9	5''	4.27 (m)	77.3
5		157.8	6''	4.71 (d, 11.0 Hz) 4.14 (m)	68.6
6	7.30 (s)	100.1	1'''	5.70 <sup>a</sup> (d, 2.5 Hz)	111.0
7		157.2	2'''	4.32 (m)	78.4
8		130.0	3'''		80.2
8a		150.9 <sup>b</sup>	4'''	4.63 (d, 9.0 Hz) 4.36 (m)	75.0
1'		111.3	5'''	4.20 (t, 11.5 Hz)	65.6
2'		152.6	5-OH	13.20 (s)	
3'	6.78 (s)	98.9	8-OCH <sub>3</sub>	3.99 (s)	61.5
4'		150.9 <sup>b</sup>	2'-OCH <sub>3</sub>	3.73 (s)	55.9
5'		143.6	4'-OCH <sub>3</sub>	3.80 (s)	56.3
6'	7.21 (s)	117.0	5'-OCH <sub>3</sub>	3.83 (s)	56.7
1''	5.68 <sup>a</sup> (d, 7.5 Hz)	102.2			

<sup>a</sup>the assignments by HSQC and HMBC correlations, <sup>b</sup>May be interchangeable.

**Table 2**  $^1\text{H}$  and  $^{13}\text{C}$ -NMR data of compound **2**

Position	$\delta_{\text{H}}$ ( $J$ in Hz)	$\delta_{\text{C}}$
2		88.27
2-CH <sub>3</sub>	1.35 (s)	22.39
3	1.91 (m) 2.31 (m)	28.12
4	2.62 (m)	29.05
5		178.42
2'	4.10 (dd, 3.0, 10.0)	83.57
3'	1.70 (m) 1.99 (m)	26.70
4'	1.76 (m) 1.95 (m)	36.87
5'	-	83.16
5'-CH <sub>3</sub>	1.28 <sup>a</sup> (s) 1.30 <sup>a</sup> (s)	25.71
6'	5.97 (dd, 11.0, 17.5)	143.67
7'	5.18 (d, 17.5) 4.99 (d, 10.5)	110.62

<sup>a</sup>May be interchangeable

667 [M-H]<sup>-</sup>;  $^1\text{H}$ -NMR (500 MHz, C<sub>5</sub>D<sub>5</sub>N,  $\delta_{\text{H}}$  ppm) and  $^{13}\text{C}$ -NMR (125 MHz, C<sub>5</sub>D<sub>5</sub>N,  $\delta_{\text{C}}$  ppm); the corresponding data are given in Table 1.

2,5'-Dimethyl-5'-vinylhexahydro-2,2'-bifuran-5(2*H*)-one (**2**): Yellowish amorphous powder;  $[\alpha]_{\text{D}}^{25} = -1.2$  (*c* 1.1, MeOH), IR (film): 2973.7, 1771.3, 1607.4, 1452.1, 1271.8, 1163.8, 1084.8, 944.9, 914.1, 829.2, 715.5, 617.1, 598.8, 564.1 cm<sup>-1</sup>; UV  $\lambda_{\text{max}}$  (MeOH) nm (log  $\epsilon$ ): 206.5 (2.462), 257.5 (1.339); HR-EI-MS:  $m/z$  [M]<sup>+</sup> 210.1254 (calcd. for C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>; found: 210.1253), EI-MS:  $m/z$  [M]<sup>+</sup> 210;  $^1\text{H}$ -NMR (500 MHz, CD<sub>3</sub>OD,  $\delta_{\text{H}}$  ppm) and  $^{13}\text{C}$ -NMR (125 MHz, CD<sub>3</sub>OD,  $\delta_{\text{C}}$  ppm); the corresponding data are given in Table 2.

## Acid hydrolysis of compound **1**

Acid hydrolysis of **1** was performed according to the procedure of Cuong and partners (Cuong et al. 2015). Briefly, compound **1** (0.85 mg) was added into 1 N HCl (2 mL) and then heated to 80 °C for 3.0 h. The acidic solution was extracted with chloroform (2 mL  $\times$  2 times). The organic layer was washed with distilled water (2 mL  $\times$  3 times), dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated to give an aglycone (0.45 mg) as a white amorphous powder. The aglycone was identified as isocaviunin by NMR spectroscopy techniques and HR-ESI-MS:  $m/z$  397.0872 (100%) [M + Na]<sup>+</sup> (calcd. for C<sub>18</sub>H<sub>19</sub>O<sub>8</sub>Na 397.0899); R<sub>f</sub> (TLC): 0.4 (CH<sub>2</sub>Cl<sub>2</sub>-MeOH, 6:1).

## Results and discussion

Compound **1** was obtained as white amorphous powder. Its molecular formula C<sub>30</sub>H<sub>36</sub>O<sub>17</sub> was deduced from its quasi-molecular ion peak at  $m/z$  707.1577 [M + K]<sup>+</sup> in its positive HR-FAB-MS data and from the  $m/z$  707 [M + K]<sup>+</sup>, 669 [M + H]<sup>+</sup>, and 667 [M-H]<sup>-</sup> peaks in its positive (negative) FAB-MS data. The IR spectrum of **1** showed absorption bands at 3510, 3378, 1654, and 1581 cm<sup>-1</sup>, which could be attributed to hydroxyl, chelated hydroxyl,  $\alpha,\beta$ -unsaturated carbonyl, and carbon-carbon double bond conjugated carbonyl groups, respectively. The UV spectrum of **1** showed absorption maxima at  $\lambda_{\text{max}}$  values of 205, 263 and 295 nm, which are characteristic of an isoflavone derivative (Dixit et al. 2012). The  $^1\text{H}$ -NMR spectrum of **1** displayed a

spectral pattern similar to that of isocaviunin 7-gentibioside (compound isolated from *D. sissoo*) with resonances from two components (Sharma et al. 1980), which include an isocaviunin nucleus [5-OH ( $\delta_{\text{H}}$  13.20, 1 H, s), H-2 ( $\delta_{\text{H}}$  8.24, 1 H, s), H-6 ( $\delta_{\text{H}}$  7.30, 1 H, s), H-6' ( $\delta_{\text{H}}$  7.21, 1 H, s), H-3' ( $\delta_{\text{H}}$  6.78, 1 H, s), 8-OCH<sub>3</sub> ( $\delta_{\text{H}}$  3.99, 3 H, s), 5'-OCH<sub>3</sub> ( $\delta_{\text{H}}$  3.83, 3 H, s), 4'-OCH<sub>3</sub> ( $\delta_{\text{H}}$  3.80, 3 H, s), and 2'-OCH<sub>3</sub> ( $\delta_{\text{H}}$  3.73, 3 H, s)] and an  $\beta$ -D-apiofuranosyl-(1  $\rightarrow$  6)- $\beta$ -D-glucopyranosyl moiety [H-1''' ( $\delta_{\text{H}}$  5.70, d, 2.5 Hz), H-1'' ( $\delta_{\text{H}}$  5.68, d, 7.5 Hz), and 11 H ( $\delta_{\text{H}}$  3.99-4.78)] (Table 1 and Fig. 1). The <sup>13</sup>C-NMR and <sup>1</sup>H-<sup>13</sup>C HSQC spectra of **1** (C<sub>5</sub>D<sub>5</sub>N) contained 30 carbon signals (12  $\times$  C, 11  $\times$  CH, 3  $\times$  CH<sub>2</sub>, 4  $\times$  CH<sub>3</sub>), which were assignable to an isoflavone aglycone, a  $\beta$ -D-apiofuranosyl residue, and a  $\beta$ -D-glucopyranosyl bridge (Table 1 and Fig. 1). Regarding the 2D-NMR analysis, the <sup>1</sup>H-<sup>13</sup>C HMBC spectrum established the isocaviunin ring by the *J*<sup>2</sup> and *J*<sup>3</sup> correlations H-2/C-3, C-4 and C-8a; H-6/C-4a, C-5, C-7, and C-8; 5-OH/C-4a, and C-5; H-3'/C-1', and C-5'; H-6'/C-5', and C-3; 8-OCH<sub>3</sub>/C-8; 2'-OCH<sub>3</sub>/C-2; 4'-OCH<sub>3</sub>/C-4; and 5'-OCH<sub>3</sub>/C-5, and a glycone unit was confirmed by the cross peaks H-2''/C-3''; H-3''/C-4''; H-4''/C-1''; and C-2''; and H-5''/C-4'' in the <sup>1</sup>H-<sup>13</sup>C HMBC spectrum, as well as H-1''/H-2''; H-4''/H-5''; H-5''/H-6''; and H-1'''/H-2''' in the <sup>1</sup>H-<sup>1</sup>H COSY spectrum (Fig. 2). Furthermore, the key <sup>1</sup>H-<sup>13</sup>C HMBC correlation H-1'''/C-6'' evidently generated a 1  $\rightarrow$  6 linkage between two sugar units, and the cross peak H-1''/C-7 indicated the connection between glycone and aglycone at C-7. In addition, the acid hydrolysis of **1** yielded the aglycone, the NMR and MS data of which were identical to those of isocaviunin (Sharma et al. 1980). Based on these data, compound **1** was elucidated to be isocaviunin-7-*O*- $\beta$ -D-apiofuranosyl-(1  $\rightarrow$  6)- $\beta$ -D-glucopyranoside.

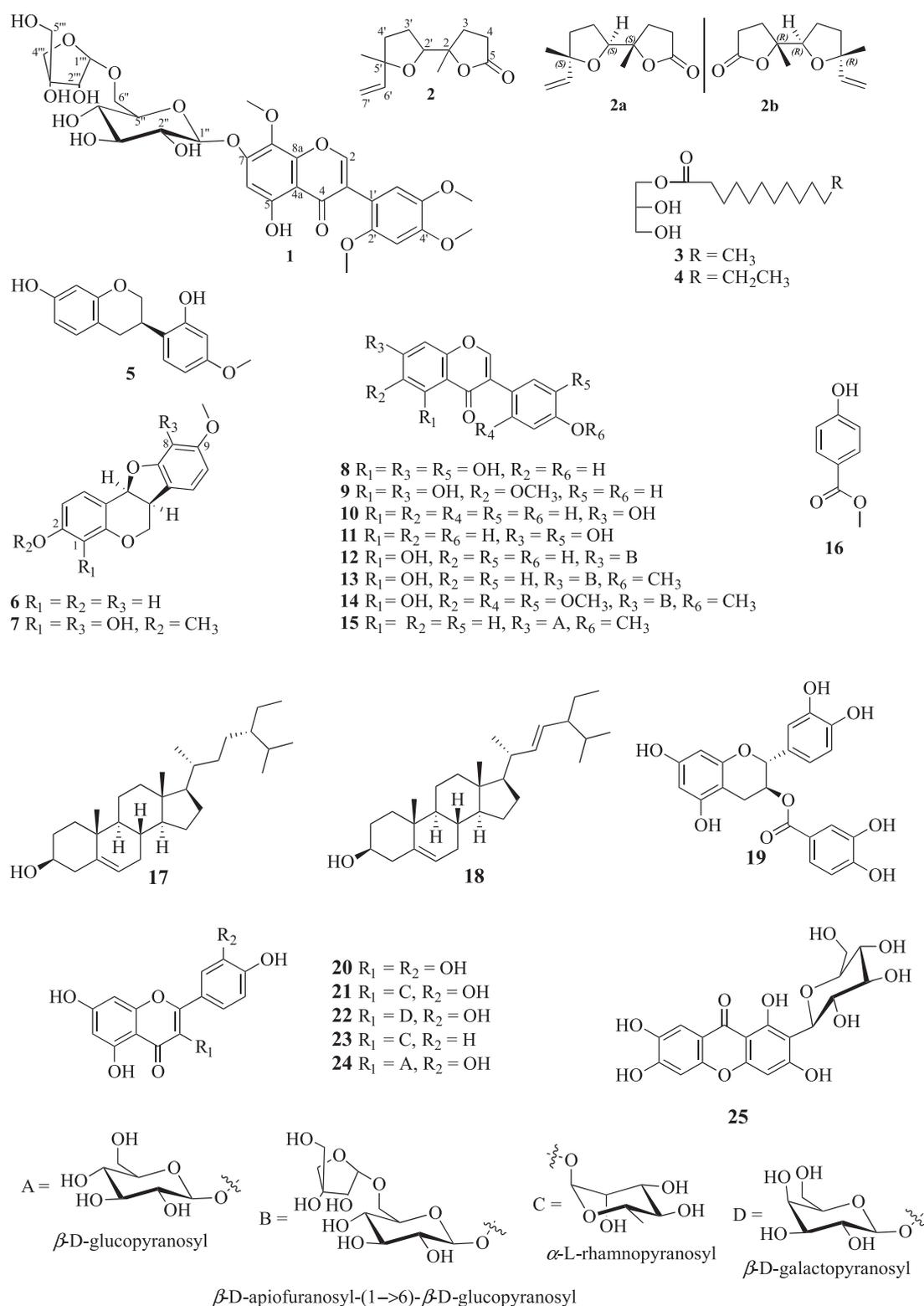
Compound **2** was obtained as yellowish amorphous powder. The molecular formula of **2** corresponded to C<sub>12</sub>H<sub>18</sub>O<sub>3</sub>, as deduced from its molecular ion peak at *m/z* 210.1253 [M]<sup>+</sup> in its positive HR-EI-MS data, as well as the peak *m/z* 210 [M]<sup>+</sup> in its positive EI-MS data. The absorptions at 1771 and 1607 cm<sup>-1</sup> in the IR spectrum showed the presence of a  $\gamma$ -lactone and a double bond, respectively. The <sup>1</sup>H and <sup>13</sup>C-NMR data of **2** were included two methine groups, five methylene groups, two methyl groups, two oxygenated quaternary carbons, and one lactone carbon (Table 2 and Fig. 1). Based on the HSQC, HMBC, COSY, and NOESY extensive analysis and comparison with the literature (Wang et al. 2014), compound **2** was assigned as a diastereomeric isomer of *rel*-(2*R*,2'*R*,5'*S*)-2,5'-dimethyl-5'-vinylhexahydro-2,2'-bifuran-5(2*H*)-one (a component was isolated from *D. odorifera* T. Chen) (Wang et al. 2014). As shown in Fig. 2, the appearance of tetrahydrofuran (THF) and  $\gamma$ -lactone rings was confirmed by the COSY correlations H-3/H-4, H-2'/H-3', and H-3'/H-4', as well as the HMBC cross peaks H-3 and H-4/C-5 and

H-4'/C-5'. Furthermore, the COSY correlation H-6'/H-7' and the HMBC interactions H-6'/C-5'; 5'-CH<sub>3</sub>/C-5' and C-4'; and 2-CH<sub>3</sub>/C-2 and C-3 indicated that the vinyl group occurred at C-5', and two methyl groups were attached at the C-2 and C-5' positions. The connection between the THF ring and the  $\gamma$  lactone ring can be explained by the key correlation 2-CH<sub>3</sub>/C-2'. In contrast to *rel*-(2*R*,2'*R*,5'*S*)-2,5'-dimethyl-5'-vinylhexahydro-2,2'-bifuran-5(2*H*)-one, H-2' had no NOE on 5'-CH<sub>3</sub>; therefore, H-2' and the 5'-methyl group were *trans*-orientated in compound **2** (Marshall and Hann 2008; Wang et al. 2014).

Compound **2** was found to have a small optical rotation of -1.2 (*c* 1.1, MeOH) (Deng et al. 2017; Song et al. 2018). As a consequence, we concluded that compound **2** was an enantiomeric mixture. Thus, compound **2** was further analyzed by a chiral HPLC column (OD-RH, 150  $\times$  4.6 mm) with a mobile phase of *n*-hexane-2-propanol (80:20, v/v), thereby showing two peaks at *t*<sub>R</sub> = 11.2 (35%) and *t*<sub>R</sub> = 15.81 (65%) (Fig. S14). Therefore, compound **2** was identified as a scalemic mixture of the two enantiomers *rel*-(2*S*,2'*S*,5'*S*)-2,5'-dimethyl-5'-vinylhexahydro-2,2'-bifuran-5(2*H*)-one (**2a**) and *rel*-(2*R*,2'*R*,5'*R*)-2,5'-dimethyl-5'-vinylhexahydro-2,2'-bifuran-5(2*H*)-one (**2b**).

Apart from the new isoflavone glycoside **1** and new scalemic mixture **2**, based on comparing their NMR spectroscopic data with the previous literature, thirteen known compounds **3-16** were also identified, including two monoacylglycerides 1-monolaurin (**3**) and 1-monomyristin (**4**); one isoflavan (3*R*)-vestitol (**5**); two pterocarpan medicarpin (**6**) and melilotolcarpan D (**7**); eight isoflavones and isoflavone glycosides orobol (**8**), tectorigenin (**9**), daidzein (**10**), 3'-hydroxydaidzein (**11**), ambocin (**12**), biochanin A-7- $\beta$ -D-apiofuranosyl-(1  $\rightarrow$  6)- $\beta$ -D-glucopyranoside (**13**), dalsissooside (**14**), and formononetin-7-*O*- $\beta$ -D-glucopyranoside (**15**); and one mono-phenol killitol (**16**) (Cho et al. 2014; Dixit et al. 2012; Lotti et al. 2010; Parthasarathy et al. 1974; Romo et al. 2018; Saha et al. 2013; Shimada et al. 1997; Zhao et al. 2011). All of the known compounds **3-16** were isolated from *D. tonkinensis* species for the first time. 1-Monolaurin (**3**), 1-monomyristin (**4**) and killitol (**16**) were never isolated from the family Fabaceae before. Ambocin (**12**) had been reported in the family Fabaceae, but this is the first time it was found in the genus *Dalbergia*.

In current paper, our phytochemical work also resulted in the appearance of two phytosterols  $\beta$ -sitosterol (**17**) and stigmasterol (**18**); one flavan (+)-catechin-3-*O*-(3,4-dihydroxybenzoyl) (**19**); four flavonol and flavonol glycosides quercetin (**20**), quercitrin (**21**), hyperin (quercetin-3-*O*- $\beta$ -galactopyranoside) (**22**), afzelin (**23**), and isoquercetin (quercetin-3-*O*- $\beta$ -glucopyranoside) (**24**); and one xanthone glycoside mangiferin (**25**) from the leaves of *C. formosum* (Choi et al. 2012; Khanam,

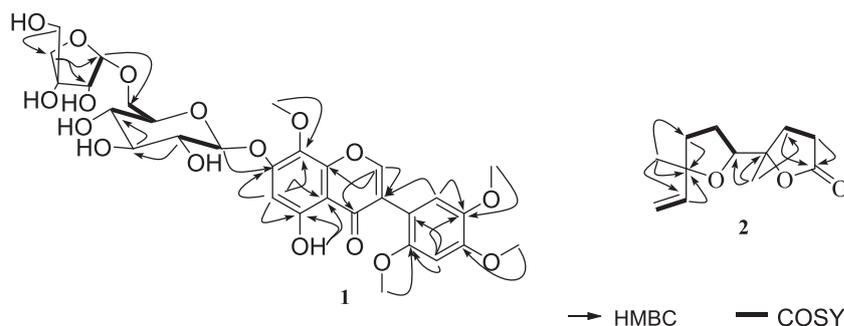


**Fig. 1** Structures of isolated compounds

Sultana (2012); Kitanov et al. 1988; Mai 2017; Tung et al. 2008). It should be noted that flavan **19** was found in genus *Cratoxylum* for first time.

The DPPH radical scavenging assay was carried out on several isolated compounds according to the protocol described by Tram and partners (Tram et al. 2017), and the

**Fig. 2** Structures and HMBC and COSY key correlations of compounds **1-2**



**Table 3** DPPH radical scavenging activity

Compounds	IC <sub>50</sub> (μg/mL)
(3 <i>R</i> )-Vestitol ( <b>5</b> )	42.20
Medicarpin ( <b>6</b> )	69.45
Melitocarpin D ( <b>7</b> )	54.14
Orobol ( <b>8</b> )	91.18
Catechin-3- <i>O</i> -(3,4-dihydroxybenzoyl) ( <b>19</b> )	75.37
Quercetin ( <b>20</b> )	66.54
Hyperin ( <b>22</b> )	66.22
Afzelin ( <b>23</b> )	> 100
Isoquercetin ( <b>24</b> )	45.63
Magniferin ( <b>25</b> )	64.03
Catechin	42.98

results are given in Table 3. With regards to several tested compounds from *D. tonkinensis* species, (3*R*)-vestitol (**5**) possessed the strongest antioxidative IC<sub>50</sub> value of 42.20 μg/mL, which was comparable to that of the positive control catechin (IC<sub>50</sub> 42.98 μg/mL). Pterocarpin **7** revealed a strong IC<sub>50</sub> value of 54.14 μg/mL when compared with the moderate IC<sub>50</sub> value of 69.45 μg/mL of pterocarpin **6** and the weak one of 91.18 μg/mL of isoflavone **8**. It can therefore be concluded that isoflavans from *D. tonkinensis* species should be the best choice for an antioxidant model compared with pterocarpanes or isoflavones. In addition, comparing the two pterocarpanes medicarpin (**6**) and melitocarpin D (**7**), hydroxylation occurred at carbons C-1 and C-8, and methoxylation happened at carbon C-2, which can be claimed to be responsible for the antioxidant increase.

Regarding the isolated compounds from *C. formosum* leaves, the IC<sub>50</sub> values established a consistent arrangement as follows: catechin (IC<sub>50</sub> 42.98 μg/mL) > isoquercetin **24** (IC<sub>50</sub> 45.63 μg/mL) > magniferin **25** (IC<sub>50</sub> 64.03 μg/mL) > hyperin **22** (IC<sub>50</sub> 64.22 μg/mL) > quercetin (**20**) (IC<sub>50</sub> 64.54 μg/mL) > catechin-3-*O*-(3,4-dihydroxybenzoyl) **19** (IC<sub>50</sub> 75.37 μg/mL) > afzelin **23** (IC<sub>50</sub> > 100 μg/mL, inactive). As a consequence, flavonols, flavonol glycosides, and xanthone glycosides may be thought of as promising antioxidant agents, but the flavans cannot be considered as such. Taking flavonol derivatives into consideration, a

glucose moiety and hydroxyl groups attached at C-3 and C-3' caused an increase in the antioxidant capacity. Similarly, 3-glucopyranosylated flavonol (compound **24**) showed a better antioxidant potency than 3-galactopyranosylated flavonol (compound **22**).

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### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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