TẠP CHÍ KHOA HỌC ĐẠI HỌC TÂN TRÀO

ISSN: 2354 - 1431

http://tckh.daihoctantrao.edu.vn/

ISOLATION AND STRUCTURAL DETERMINATION OF ISOFLAVANONES FROM DALBERGIA TONKINESIS PRAIN COLLECTED IN DAK LAK

Dam Thi Bich Hanh[1], Nguyen Phu Khanh[2], Dang Thi Thuy My[1], Le Thi Thuy Loan[1], Nguyen Thi Van Dung[1], Le Hong Thuy[1], Phan Hoang Thai Bao[1]*

[1]Faculty of Science and Technology, Tay Nguyen University, Buon Ma Thuot, Daklak, Vietnam

[2]Military Hospital 175, Ho Chi Minh City, Vietnam

Email address: phtbao@ttn.edu.vn

https://doi.org/10.51453/2354-1431/2023/1012

Article info

Received:5/4/2023

Revised: 18/6/2023

Accepted: 8/8/2023

Keywords

Dalbergia tonkinensis, Fabaceae, flavonoids, wood.

Abstract

From the ethyl acetate extract of the wood of *Dalbergia tonkinensis* Prain, was collected in Buon Ma Thuot city, DakLak provice, two isoflavanones sativanone (**1**), and 3'-*O*-methylviolanone (**2**) were isolated. The chemical structure of these compounds were determined by the interpretation of NMR spectral data and comparison with published data. This is the first time they are reported from wood of *Dalbergia tonkinensis*.

TẠP CHÍ KHOA HỌC ĐẠI HỌC TÂN TRÀO
ISSN: 2354 - 1431
http://tckh.daihoctantrao.edu.vn/

PHÂN LẬP VÀ XÁC ĐỊNH CẤU TRÚC DALBERGIN TỪ CÂY SƯA (DALBERGIA TONKINESIS PRAIN) Ở ĐẮK LẮK

Đàm Thị Bích Hạnh[1], Nguyễn Phú Khanh[2], Đặng Thị Thuỳ My[1], Lê Thị Thuý Loan[1], Nguyễn Thị Vân Dung[1], Lê Hồng Thuý[1], Phan Hoàng Thái Bảo[1]*

[1]Trường Đại học Tây Nguyên, Việt Nam

[2]Bệnh viện Quân Y 175, Thành phố Hồ Chí Minh, Việt Nam

Địa chỉ email: phtbao@ttn.edu.vn

https://doi.org/10.51453/2354-1431/2023/1012

Thông tin bài viết

Ngày nhận bài: 5/4/2023

Ngày sửa bài: 18/6/2023

Ngày duyệt đăng: 8/8/2023

Tóm tắt

Từ cao ethyl axetat của cây Sưa (*Dalbergia tonkinensis* Prain) thu được tại thành phố Buôn Ma Thuột, tỉnh Đắc Lắc, đã phân lập được hai hợp chất isoflavanone: sativanone (**1**) và 3'-O-methylviolanone (**2**). Cấu trúc hóa học của các hợp chất này được xác định bằng phổ cộng hưởng từ hạt nhân (NMR) đồng thời đối chiếu với các tài liệu tham khảo đã công bố. Đây là lần đầu tiên chúng được phân lập từ loài *Dalbergia tonkinensis*.

Từ khóa

Dalbergia tonkinensis, Fabaceae, flavonoid, cây Sưa

1. Introduction

There are over 310 recognized species in the *Dalbergia* genus, belonging to the family Fabaceae, are found widely distributed in tropical and subtropical regions [1]. In Vietnam the *Dalbergia* genus approximately 30 species. Most species in the *Dalbergia* genus have been widely used since in the long time in many countries to treat conditions such as nosebleeds, diarrhea, headache, syphilis, coughs, infections, fractures, fever scabies, worms, rheumatism, anti-inflammatory, antibacterial, absent-mindedness, blood pressure, etc [2, 3, 4].

Various biological activities of the Dalbergia species have reported, including antimicrobial, antidiarrheal, anti-cancer, spermicidal, anti-inflammatory, antipyretic, analgesic, and cardiovascular activity [5]. In addition. Phytochemical studies of the genus Dalbergia have indicated that its chemical constituents are various flavonoids as flavones, isoflavones, neoflavones, flavanones, isoflavanones, flavanes, isoflavanes, neoflavans, 4-aryl-coumarins, phenols, sesquiterpenes, phytosterols, together coumaronochromone derivatives [6, 7, 8]

The *Dalbergia tonkinensis* Prain species (commonly called 'Sua Do'), is a medium-size floral species 5-13 meters, is widely distributed scattered from North to Sonth in Vietnam and is classified as precious tree species listed in the Red Book.This is rare spices with high valuable economic [9, 10]

Previous studies have reported on the chemical constituent from the heartwood of the *Dalbergia tonkinensis* have carried by N.M.Cuong et al, two new carboxyethylflavanones: daltonkin (A), daltonkin (B), and neoflavonoid were isolated [5, 6]. In this paper, we describle the isolate and structural elucidation of two compounds, sativanone (**1**), and 3'-*O*-methylviolanone (**2**) from the wood of this species.

2. Experimental

2.1. Plant material

The plant and wood of *D. tonkinensis* Prain was collected in Buon Ma Thuot city, Daklak province, Vietnam in 2018. Its scientific name was identified by botanist Dr. Nguyen Quoc Binh, Vietnam National Museum of Nature, VAST, Hanoi, Vietnam. A voucher specimen (Sua Do-SD-Go) is deposited with the Natural Product Chemistry Lab, Tay Nguyen University.

2.2. General Experimental Procedures

The ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) were measured on a Bruker Avance 500 MHz spectrometer. Column chromatography was carried out on silica gel (Si 60 F_{254}, 40-63 mesh, Merck, St. Louis, MO, USA). All solvents were redistilled before use. Pre-coated TLC plates (Si 60 F_{254}) were used for analytical purposes. Compounds were visualized under UV radiation (254, 365 nm) and by spraying plates with 10% H_2SO_4 followed by heating with a heat gun.

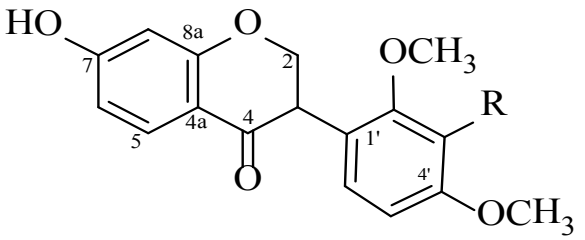
2.3. Extraction and Isolation

Dried powdered woods (3.7 kg) of *D. tonkinensis* were extracted with hot methanol (5 x 7.0 l) under reflux, filtered, and then concentrated under decreased pressure giving a black crude methanol residue (120 g). The suspension of the methanol residue in hot methanol-water (1:1, v/v) was successively partitioned with *n*-hexane, dichloromethane and ethyl acetate to give *n*-hexane (29.0 g, MH), dichloromethane (45.1 g, MD), ethyl acetate (11.1 g, ME) and water (12.0 g, MW) fractions, respectively.

The fraction ME (11.1 g) was chromatographed on a normal silica gel (40-63 mesh) chromatography column (CC) using a gradient of chloromethane and acetone as eluent to afford 12 fractions (ME1-ME12). Fraction ME1 (500 mg) was rechromatographed on a normal silica gel CC (chloroform-acetone 99-1 as eluent, v/v) to produce 8 sub-fractions (ME1.1- ME1.8). The sub-fraction ME1.4 (240 mg) was further separated on a normal silica gel CC, eluting with *n*-hexane-ethyl acetate (8:1, v/v) to obtain compound **1** (6 mg). Fraction ME5 (310 mg) was rechromatographed on a normal silica gel CC (chloroform- ethylacetate 4-1 as eluent, v/v) to produce 15 sub-fractions (ME4.1-ME4.15). Compound **2** (12.0 mg) was obtained from the sub-fraction ME4.10.

Sativanone (1): white amorphous power ($C_{17}H_{16}O_5$, M = 300). ^{1}H-NMR (500 MHz, CD_3OD): ^{1}H-NMR (500 MHz, CD_3OD): 7.78 (1H, d, 8.5, H-5), 7.00 (1H, d, 8.5, H-6'), 6.58 (1H, d, 2.5, H-8), 6.52 (1H, dd, 8.5, 2.5, H-6), 6.49 (1H, dd, 8.5, 2.5, H-5'), 6.35 (1H, d, 2.5, H-3'), 4.56 (1H, t, 11.5, H_a-2), 4.40 (1H, dd, 11.5, 5.5, H_b-2), 4.17 (1H, dd, 11.5, 5.5, H-3), 3.80 (3H, s, 2'-OCH_3), 3.78 (3H, s, 4'-OCH_3). ^{13}C-NMR (125 MHz, CD_3OD): 194.4 (s, C-4), 166.4 (s, C-7), 165.8 (s, C-8a), 162.2 (s, C-4'), 159.9 (s, C-2'), 132.0 (d, C-5), 130.4 (d, C-6'), 117.4 (s, C-1'), 111.7 (d, C-3'), 106.0 (d, C-5'), 103.6 (d, C-6), 115.7 (s, C-4a), 99.9 (d, C-8), 70.0 (t, C-2), 56.6 (q, 4'-OCH_3), 55.8 (q, 2'-OCH_3), 49.7 (d, C-3).

3'-*O*-methylviolanone (2): white amorphous power ($C_{18}H_{18}O_6$, M = 330). ^{1}H-NMR (500 MHz, CD_3OD): 6.54 (1H, d, 8.5, H-5), 6.86 (1H, d, 8.5, H-6'), 6.36 (1H, d, 2.5, H-8), 6.54 (1H, dd, 8.5, 2.5, H-6), 6.75 (1H, dd, 8.5, H-5'), 4.55 (1H, t, 11.5, H_a-2), 4.15 (1H, dd, 11.5, 5.5, H_b-2), 4.44 (1H, dd, 11.5, 5.5, H-3), 3.82(3H, s, 4'-OCH_3), 3.83 (3H, s, 2'-OCH_3), 3.85 (3H, s, 4'-OCH_3). ^{13}C-NMR (125 MHz, CD_3OD): 194.2 (s, C-4), 166.5 (s, C-7), 165.8 (s, C-8a), 155.1 (s, C-4'), 153.2 (s, C-2'), 130.4 (d, C-5), 126.0 (d, C-6'), 123.1 (s, C-1'), 143.6 (d, C-3'), 106.8 (d, C-5'), 111.8 (d, C-6), 115.6 (s, C-4a), 103.7 (d, C-8), 72.3 (t, C-2), 61.2 (q, 3'-OCH_3), 61.0 (q, 2'-OCH_3), 56.0 (q, 4'-OCH_3), 49.7 (d, C-3).



1 R = H
2 R = OCH_3

Figure 1. Chemical structure of isolated compounds 1-2 from the wood of *D. tonkinensis*.

3. Results and discussion

Compound **1** was obtained as white amorphous powder. The ^{1}H-NMR of **1** showed three protons in AMX spin system at δ_H 4.40 (1H, dd, J = 11.5, 5.5 Hz), 4.56 (1H, t, J=11.5 Hz) and 4.17 (1H, dd, J = 11.5, 5.5 Hz), typically assignable to H-2 and H-3 of isoflavanone skeleton.

Besides, the ^{1}H-NMR spectrum also supported the presence of two methoxy group at δ_H 3.80 (3H, s, 2'-OCH_3) and 3.78 (3H, s, 4'-OCH_3).

The ^{13}C-NMR and DEPT spectrum showed signals for seventeen carbons: a carbonyl carbons at δ_C 194.4 (C-4), six aromatic quaternary carbons at δ_C 164.4 (s, C-7), 165.8 (s, C-8a), 162.2 (s, C-4'), 159.9 (s, C-2'), 117.4 (s, C-1'), 115.7 (s, C-4a) and six arometic methine carbons at δ_C 132.0 (d, C-5), 103.6 (d, C-6), 130.4 (d, C-6'), 99.9 (d, C-8), 111.7 (d, C-3') and 106.0 (d, C-5') together with an signal oxy methylenen carbon at δ_C 70.0 (t, C-2), a methine carbon δ_C 49.7 (d, C-3), two methoxy group δ_C 56.6 (q, 4'-OCH_3) and 55.8 (q, 2'-OCH_3). In the ^{13}C-NMR spectrum suggested the prescence of a isoflavanone skeleton. On the basis of above discussion and comparison with literature data [11], has identified **1** as sativanone. This compound was previously isolated from heartwood of *Dalbergia odorifera* [3].

Table 1. ^{1}H NMR and ^{13}C NMR spectroscopic data for 1 and reference compound.

Position	1 (*)		Sativanone [11]	
	δ_H (ppm) (J inHz)	δ_C (ppm)	δ_C	δ_H
1	-	-	-	-
2	4.40, dd, 11.5, 5.5 4.56, t, 11.5	72.1	70.2	4.40, dd, 11.0, 5.5 4.54, d, 11.0
3	4.17, dd, 11.5, 5.5	49.7	47.5	4.16, dd, 11.0, 5.5
4	-	194.4	192.4	-
4a	-	115.7	113.7	-
5	7.78, d, 8.5	132.0	129.9	7.76, d, 8.7
6	6.52, dd, 8.5, 2.5	103.6	101.8	6.49, d, 8.7
7	-	166.4	164.2	-
8	6.58, d, 2.5	99.9	98.0	6.51, s
8a	-	165.8	163.6	-
1'	-	117.4	115.3	-
2'	-	159.9	157.7	-
2'-OCH_3	3.80, s	55.8	54.0	3.77, s
3'	6.35, d, 2.0	111.7	109.8	6.33, d, 2.3
4'	-	162.2	160.0	-
4'-OCH_3	3.78	56.0	54.2	3.74, s
5'	6.49, dd, 8.5, 2.5	106.0	104.0	6.46, dd, 8.4, 2.3
6'	7.00, d, 8.5	130.4	128.5	6.97, d, 8.4

(*)^{1}H (500 MHz), ^{13}C (125 MHz) recorded in MeOH with TMS as an internal standard.

Compound **2** was isolated as white amorphous power. The ^{1}H-NMR spectrum exhibited similar signals of ring A of Compound **1.** The difference was the presence of two ortho-couped protons of ring B at δ_H 6.86 (1H, d, J = 8.5 Hz, H-6') and 6.75 (1H, dd, J = 8.5 Hz, H-5'). Thurthermore, The ^{1}H-NMR spectrum also supported the presence of a methoxy group with a singlet signal at δ_H 3.82 (q, 3'-OCH_3)and 6.37 (1H, d, J = 2.5 Hz, H-8).

The ^{13}C-NMR and DEPT spectra of compound **1** are similar of compound **1.** The difference was the presence of a signal methoxy group at δ_C 61.2 (q, 3'-OCH_3) due to replacement of the aromatic proton H-3' in Compound **2** by a methoxy group, so showed signals an aromatic quaternary carbons at δ_C 143.6 (s, C-3'). Combined analysis of (^{1}H-, ^{13}C-NMR) and comparison with published data verified the compound **2** was established 3'-*O*-methylviolanone [12].

Table 2. ^{1}H NMR and ^{13}C NMR spectroscopic data for 2 and reference compound.

Position	2 (*)		3'-*O*-methylviolanone [12]	
	δ_H (ppm) (J inHz)	δ_C (ppm)	δ_C	δ_H
1	-	-	-	-
2	4.55, t, 11.5 4.15, dd, 11.5, 5.5	72.3	4.52, dd, 11.2, 5.2 4.15, dd, 11.2, 5.2	71.1
3	4.44, dd, 11.5, 5.5	49.7	4.45, dd, 11.2, 5.2	47.8
4	-	194.2	-	190.9
4a	-	115.6	-	114.3
5	7.79, d, 8.5	130.4	7.69, d, 8.8	129.4
6	6.54, dd, 8.5, 2.5	111.8	6.54, dd, 8.8, 2.4	111.1
7	-	166.5	-	164.8
8	6.36, d, 2.5	103.7	6.36, d, 2.4	102.8
8a	-	165.8	-	163.7
1'	-	123.1	-	122.1
2'	-	153.2	-	151.9
2'-OCH_3	3.83, s	61.0	3.74, s	60.6
3'	-	143.6	-	142.2
3'-OCH_3	3.82, s	61.2	3.71, s	60.9
4'	-	155.1	-	153.5
4'-OCH_3	3.85, s	56.6	3.78, s	56.3
5'	6.75, d, 8.5	108.8	6.76, d, 8.8	108.2
6'	6.86, d, 8.5	126.0	6.85, d, 8.8	124.9

(*)^{1}H (500 MHz), ^{13}C (125 MHz) recorded in MeOH with TMS as an internal standard.

4. Conclusions

By various choromatographic, two flavonoids, sativanone (**1**), and 3'-*O*-methylviolanone (**2**) were isolated from the ethyl acetatel extract of wood of *Dalbergia tonkinenensis* was collected in Buon Ma Thuot city, DakLak provice. Their chemical structures were determined by the interpretation of NMR spectral data and comparison with published data. Althought these compounds were already reported in many different species, but this is the first time they are confirmed from wood of *Dalbergia tonkinensis*.

REFERENCES

[1] The Plant List. Available: http://www.theplantlist.org/tpl1.1/search?q=dalbergia, (Accessed, July 29, 2017)

[2] Chi V.V.- Dictionary of Vietnamese Medical plants, Medical Publishing Huose, 2(2012) 1047-1054.

[3] Sanjib S., Jamil A. S., Himangsu M., Faroque H., Md. Anisuzzman, Md. Mahadhi H., Geoffrey A. C. (2013) *Ethnomedicinal, phytochemical, and pharmacological profile of the genus Dalbergia L. (Fabaceae)*. Phytopharmacology **4** , 291-346.

[4] Nhan, N.T., Nguyen, P.H., Hanh, D.T.B., My, D.T.T., Nguyen, N.P.D., Phong, T.B., Huong, N.T.M., Hung, T.M., Tram, N.T.T., & To, D.C. (2022) Anti-inflammatory activity of ingredients from the heartwood of Vietnamese *Dalbergia oliveri* Gamble ex, *European Journal of Inflammation*, 20, 1-8.

[5] Cuong, N.M., Son, N.T., Nhan, N.T., Yoshiyasu Fukuyama, Amer Ahmed, Simona Saponara, Alfonso Trezza, Beatrice Gianibbi, Ginevra Vigni, Ottavia Spiga and Fabio Fusi, (2022) Vietnamese *Dalbergia tonkinensis*: A Promising Source of Mono-and Bifunctional Vasodilators, *Molecules* , *27(14)*, 4505.

[6] Cuong N.M., Nhan N.T., Son N.T., Nghi D.H., Cuong T.D. (2017). DaltonkinA and B, two new carboxyethylflavanone from the heartwood

of *Dalbergia tonkinensis*. Bull.Korean.Chem.Soc. 38(12),P.1511-1514.

[7] Ho P.H- AnIllus trated Flora of Vietnam, 2nded, Youth Publisher, Ho Chi Minh City, Vietnam **1**(1999).

[8] Mai N.T.H., Cuong N.M., Nhan N.T., Nguyen N.P.D., Trang N.T.P (2017). Molecular chracteristics and classification ability of rpoc region for *Dalbergia cochinchinensis* Pierre and *Dalbergia tonkinensis* Prain species in Viet Nam. Proceedings of the 7th national scientific confercence on eology and biological resources. Journal of Science and Technology, Ha Noi, 814-817.

[9] Sorachai K., Saisunee L., Aphiwat T., Stephen G., Mary J., Boonsom L. -The isolation of bioactive flavonoids from *Jacaranda obtusifolia H. B. K*. ssp. rhombifolia (G. F. W. Meijer) Gentry. Acta Pharm. (2012), 62, 181-190.

[10] Xiao Z., Wenli M., Mingfu G., Wenjian Z., Hongjin B., Haofu D. (2011). Antibacterial activity of the flavonoids from *Dabergia oddorifera* on Ralstonia solanacearum. Molecule. 16, 9775-9782.

[11] Jin W.L., Chul L., Qing H.J., Moon S.L., Young S.K., Jin T.H., Mi K.L., Bang Y.H. (2014). Chemical constituents from *Belamcanda chinensis* and their inhibitory effects on nitric oxide production in RAW 264.7 macrophage cells. Arch. Pharm. Res. 38(6), 991-997.