Chiang Mai J. Sci. 2019; 46(2) : 277-283
http://epg.science.cmu.ac.th/ejournal/
Contributed Paper

Chemical Constituents from the Twigs of *Decaneuropsis vagans* (Asteraceae) and Its Chemotaxonomic Study

Anuruk Chailungka [a,b], Puttinan Meepowpan [a,c] and Aroonchai Saiai* [a,c]

[a] Department of Chemistry, Faculty of Science, Chiang Mai University, Chiang Mai 50200, Thailand.

[b] Faculty of Engineering and Technology, North-Chiang Mai University, Chiang Mai 50230, Thailand.

[c] Center of Excellence for Innovation in Chemistry, and Research Center on Chemistry for Development of Health Promoting Products from Northern Resources, Chiang Mai University, Chiang Mai 50200, Thailand.

*Author for correspondence; e-mail: aroonchai.s@cmu.ac.th

Received: 2 August 2018
Revised: 1 September 2018
Accepted: 12 September 2018

ABSTRACT

The first phytochemical investigation of the twigs of *Decaneuropsis vagans* (DC.) H. Rob. & Skvarla. resulted in the isolation of six known compounds, including lupeol palmitate (**1**), lupeol acetate (**2**), eugenol (**3**), macelignan (**4**) and a mixture of β-sitosterol (**5**) and stigmasterol (**6**). Their structures were characterized by various spectroscopic methods and comparison with the data reported in the literature. Compounds **1**-**6** were isolated from this species for the first time and compound **4** was firstly found in the Asteraceae family.

Keywords: *Decaneuropsis vagans*, *Vernonia vagans*, *Vernonia scandens* DC., Asteraceae, chemical constituents

1. INTRODUCTION

Decaneuropsis vagans (DC.) H. Rob. & Skvarla is a new name of *Vernonia scandens* (synonymous *Vernonia vagans*). Twelve known species of genus *Vernonia* were placed to *Decaneuropsis* genus which has been a new genus since 2007 [1]. Only *Decaneuropsis cumingiana* (Benth.in Hook.f) H. Rob. & Skvarla was investigated with the name of *Vernonia cumingiana* Benth. which was reported the isolation of two stigmastane-type steroidal glycosides from its roots [2]. Therefore, this is the first time that chemical constituents of this species have been reported.

2. MATERIALS AND METHOD

2.1 Plant Material

The twigs of *D. vagans* were collected in March 2008 from the northern part of Mae Jam District in Chiang Mai of Thailand and identified by Mr. James Maxwell. A voucher specimen (MAXWELL 08-54) was deposited in the herbarium of Chiang Mai University, Thailand.

2.2 General Procedure

Melting points (m.p.) were measured on a digital electrothermal melting apparatus (SANYO 1.0 A, 220/240 v, 50(65) w). The

^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker AVANCE 400 spectrometer, operating at 400 and 100 MHz, respectively. IR spectra were obtained using FT-IR 4796 spectrometer (Bruker, TENSOR 27). High-resolution mass spectra (HRMS) were measured on a Q-TOF 2™ mass spectrometer with a Z-spray™ ES source (Micromass, Manchester, UK). UV spectra were recorded using a Lambda 25 UV/Vis spectrometer (PerkinElmer Instruments). Column chromatography was performed by using silica gel 60 (Merck No. 9385, 0.040-0.063 mm). Organic solvents were commercial grade and were distilled before using for extraction and as eluent for column chromatography.

2.3 Extraction and Isolation

The air-dried and powder twigs of *D. vagans* (2.58 kg) were sequentially macerated with CH_2Cl_2 and MeOH twice (3 days each) at room temperature, respectively. After the solvents were removed, the CH_2Cl_2 extract (28.64 g, 1.12% yield) and the MeOH extract (dark green gum, 16.32 g, 0.63% yield) were obtained respectively. The CH_2Cl_2 extract (28.64 g) was separated by column chromatography (CC) eluted with gradient mixtures of *n*-hexane, *n*-hexane-CH_2Cl_2, CH_2Cl_2-EtOAc, EtOAc-MeOH and MeOH, respectively. The same spot TLC patterns were combined together to give 9 fractions (A1-9). Fraction A2 was then separated over silica gel eluted with CH_2Cl_2:*n*-hexane (5:95) to give 4 subfractions (A2a-d). Subfraction A2c was further purified by subjecting to CC eluted with EtOH:*n*-hexane (2:98) to give 3 subfractions (A2c1-3). Subfractions A2c2 and A2c3 contained mainly solid substances and were recrystallized from the mixture of CH_2Cl_2:*n*-hexane to afford compounds **1** (176.9 mg) and **2** (56.6 mg) as white solids, respectively. Fraction A4 was subjected to further purification on silica gel column eluted with CH_2Cl_2:*n*-hexane (80:20) to give 6 subfractions (A4a-f). The subfraction A4c was further purified by preparative thin layer chromatography using acetone:*n*-hexane (2:98) as eluent to afford compound **3** as yellow oil (118.5 mg). Fraction A5 was separated on silica gel column eluted with EtOAc:*n*-hexane (5:95) to give 4 subfractions (A5a-d). Compound **4** (86.0 mg) was obtained from fraction A5c as yellow gum. Fraction A7 was further fractionated by CC using *n*-hexane, *n*-hexane-EtOAc, EtOAc-MeOH and MeOH as eluents with increasing polarity of solvents to afford 6 subfractions (A7a-f). Subfraction A7c was subjected to CC eluted with EtOAc:*n*-hexane (10:90) to give 5 subfractions (A7c1-5). Compounds **5** and **6** (1.26 g) were obtained from fraction A7c3 as white solid mixture.

Lupeol palmitate (**1**): White solid, m.p. 83.5-84.0 °C; FTIR (neat) ν_{max} 2915 (C-H), 1728 (C=O), 1641 (C=C), 1173 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.78 (3H, *s*, H-28), 0.84, 0.86, 0.88 (9H, each *s*, H-23, 24, 25), 0.88 (3H, *s*, H-16′), 0.94 (3H, *s*, H-27), 1.03 (3H, *s*, H-26), 1.68 (3H, *s*, H-30), 2.27 (2H, *t*, J = 7.2 Hz, H-2′), 2.38 (1H, *td*, J = 11.1, 5.7 Hz, H-19), 4.47 (1H, *m*, H-3), 4.57 (1H, *m*, H-29), 4.68 (1H, *m*, H-29); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.1 (C-16′), 14.5 (C-27), 16.0 (C-24), 16.2 (C-26), 16.6 (C-25), 18.0 (C-28), 18.2 (C-6), 19.3 (C-30), 20.9 (C-11), 22.7 (C-15′), 23.7 (C-2), 25.1 (C-3′), 25.2 (C-12), 27.4 (C-15), 28.0 (C-23), 29.2-29.8 (C-4′-13′), 31.9 (C-14′), 34.2 (C-7), 34.8 (C-2′), 35.6 (C-16), 37.1 (C-10), 37.8 (C-4), 38.0 (C-13), 38.4 (C-1, 21), 40.0 (C-22), 40.8 (C-8), 42.8 (C-14), 43.0 (C-17), 48.0 (C-19), 48.3 (C-18), 50.3 (C-9), 55.4 (C-5), 80.6 (C-3), 109.4 (C-29), 150.9 (C-20), 173.6 (C-1′); EIMS m/z 664 [M$^+$], 649, 621, 445, 408, 189 [3-5].

Lupeol acetate (**2**): White solid, m.p. 210.0-212.0 °C; FTIR (neat) ν_{max} 2946 (C-H), 1731 (C=O), 1641 (C=C), 1249 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.78 (1H, *m*, H-5), 0.83 (3H, *s*, H-28), 0.84 (9H, *s*, H-23, 24, 25), 0.93 (3H, *s*, H-27), 1.02 (3H, *s*, H-26), 1.68 (3H, *s*, H-30), 1.86-1.96 (2H, *m*, H-21), 2.04 (3H, *s*, H-2′), 2.38 (1H, *dt*, *J* = 11.1, 5.7 Hz, H-19), 4.47 (1H, *dd*, *J* = 10.4, 5.4 Hz, H-3), 4.56 (1H, *dd*, *J* = 2.3, 1.3 Hz, H-29), 4.68 (1H, *d*, *J* = 2.3 Hz, H-29); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 14.5 (C-27), 15.9 (C-24), 16.1 (C-25), 16.4 (C-26), 17.9 (C-28), 18.1 (C-6), 19.2 (C-30), 20.9 (C-11), 21.6 (C-2′), 23.7 (C-2), 25.0 (C-12), 27.4 (C-15), 27.9 (C-23), 29.8 (C-21), 34.2 (C-7), 35.5 (C-16), 37.0 (C-10), 37.7 (C-4), 38.0 (C-13), 38.3 (C-1), 39.9 (C-22), 40.8 (C-8), 42.8 (C-14,17), 48.0 (C-18), 48.2 (C-19), 50.3 (C-9), 55.4 (C-5), 80.9 (C-3), 109.3 (C-29), 150.9 (C-20), 171.0 (C-1′); EIMS *m*/*z* 468 [M^+], 453, 425, 408, 249, 189 [6].

Eugenol (**3**): Yellow oil; FTIR (neat) ν_{max} 3506 (O-H), 2938 (C-H), 1610 (C=C), 1268 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 3.32 (2H, *d*, *J* = 6.7 Hz, H-1′), 3.88 (3H, *s*, 2-OCH_3), 5.07 (2H, *m*, H-3′), 5.50 (1H, *brs*, 1-OH), 5.96 (1H, *m*, H-2′), 6.69 (2H, *m*, H-3, 5), 6.85 (1H, *m*, H-6); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 39.8 (C-1′), 55.8 (2-OCH_3), 111.1 (C-3), 114.2 (C-6), 115.4 (C-3′), 121.1 (C-5), 131.8 (C-4), 137.8 (C-2′), 143.8 (C-1), 146.4 (C-2); EIMS *m*/*z* 164 [M^+], 149, 137, 121 [7].

Macelignan (**4**): Yellow gum; $[\alpha]_D^{27.5}$ = +7.8° (c = 0.32, $CHCl_3$); FTIR (neat) ν_{max} 3538 (O-H), 2960 (C-H), 1608 (C=C), 1038 (C-O), 933 (O-CH_2-O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.83 (3H, *d*, *J* = 6.6 Hz, H-9), 0.85 (3H, *d*, *J* = 6.6 Hz, H-9′), 1.74 (2H, *m*, H-8,8′), 2.25 (1H, *dd*, *J* = 13.6, 9.1 Hz, H-7′), 2.29 (1H, *dd*, *J* = 13.6, 5.0 Hz, H-7), 2.72 (2H, *dd*, *J* = 13.6, 5.0 Hz, H-7,7′), 3.86 (3H, *s*, 3-OCH_3), 5.50 (1H, *brs*, 4-OH), 5.92 (2H, *dd*, 2.6, 1.4 Hz, OCH_2O), 6.61 (1H, *dd*, *J* = 8.2, 1.5 Hz, H-6), 6.62 (1H, *d*, *J* = 1.5 Hz, H-2′), 6.65 (1H, *dd*, *J* = 8.2, 1.6 Hz, H-6′), 6.66 (1H, *d*, *J* = 1.6 Hz, H-2), 6.73 (1H, *d*, *J* = 7.9 Hz, H-5), 6.83 (1H, *d*, *J* = 7.9 Hz, H-5′); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 16.1 (C-9), 16.2 (C-9′), 38.8 (C-7′), 39.0 (C-7), 39.2 (C-8′), 39.3 (C-8), 55.8 (3-OCH_3), 100.7 (OCH_2O), 107.9 (C-5), 109.3 (C-2), 111.4 (C-2′), 114.0 (C-5′), 121.7 (C-6), 121.8 (C-6′), 133.7 (C-1′), 135.7 (C-1), 143.5 (C-4′), 145.4 (C-4), 146.3 (C-3′), 147.4 (C-3); EIMS *m*/*z* 328 [M^+], 137, 135 [8].

β-Sitosterol (**5**) and stigmasterol (**6**): White amorphous solid; FTIR (neat) ν_{max} 3396 (O-H), 2937 (C-H), 1642 (C=C), 1048 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 0.69 (3H, *s*, H-18), 0.79 (3H, *d*, *J* = 7.0 Hz, H-27), 0.81 (3H, *t*, *J* = 7.0 Hz, H-29), 0.84 (3H, *d*, *J* = 6.5 Hz, H-26), 1.00 (3H, *s*, H-21), 1.02 (3H, *s*, H-19), 3.52 (1H, *m*, H-3), 5.01* (1H, *dd*, *J* = 15.2, 8.6 Hz, H-23), 5.14* (1H, *dd*, *J* = 15.2, 8.6 Hz, H-22), 5.43 (1H, *m*, H-6)* found in stigmasterol; EIMS *m*/*z* 414 and 412 [M^+] [9].*found in stigmasterol

3. RESULTS AND DISCUSSION

3.1 Structural Identification of Compounds 1-6

Compound **1** ($C_{46}H_{80}O_2$, M^+= 664) was obtained as a white solid with a melting point of 83.5-84.0 °C (from CH_2Cl_2/*n*-hexane) (lit. 78-79 °C [3], 80-81.5 °C [4]). Its IR spectrum showed the absorption bands at 1728 (C=O), 1641 (C=C) and 1173 (C-O) cm^{-1} suggesting the presence of ester and olefinic groups. The ^{1}H NMR of **1** displayed triterpenoid skeleton which has eight methyl groups at δ 0.78 (s, 28-CH_3), 0.84, 0.86, 0.88 (each *s*, 23, 24, 25-CH_3), 0.88 (*s*, 16′-CH_3), 0.94 (*s*, 27-CH_3), 1.03 (*s*, 26-CH_3) and 1.68 ppm (*s*, 30-CH_3). The signal at δ 4.47 ppm (*m*, 1H) indicated the presence of methine proton H-3 connected with ester group (Figure 1). The signals at δ 4.57 (*m*, 1H, H-29) and

4.68 ppm (*m*, 1H, H-29) suggested the presence of olefinic protons connected to a quaternary carbon. The ^{13}C NMR and DEPT experiments revealed the presence of eight methyl, twenty-five methylene, six methine and seven quaternary carbons. Comparing the ^{1}H and ^{13}C chemical shifts of **1** with lupeol palmitate, they were identical. Additionally, the fragment ion in the EI-MS at m/z 408 [M^+-$C_{16}H_{32}O_2$] confirmed the presence of palmitate moiety in **1**. By analysis of 2D NMR data and comparison data with those reported in the literature, compound **1** was identified as lupeol palmitate [3-5].

Compound **2** ($C_{32}H_{52}O_2$, M^+ = 468) was isolated as a white solid with the melting point of 210.0-212.0 °C (from EtOAc/ *n*-hexane) (lit.190-192 °C [6]). The ^{1}H NMR spectrum of **2** was similar to **1** except the number of methylene protons at 1.2-1.4 ppm and the presence of acetyl group signal at 2.04 ppm. The ^{13}C NMR and DEPT experiments revealed the presence of eight methyl, eleven methylene, six methine and seven quaternary carbons. By further analysis of 2D NMR data and by comparison of the spectroscopic data with previously reported in the literature, compound **2** was identified as lupeol acetate [6].

Compound **3** ($C_{10}H_{12}O_2$, M^+=164) was obtained as yellow oil. The IR spectrum exhibited hydroxyl group at 3506 cm^{-1}, alkene C=C and aromatic ring at 1610 cm^{-1}, and C-O stretching band around 1268 cm^{-1}. The ^{1}H NMR spectrum of compound **3** showed signal of substituted aromatic ring at δ 6.69 (2H, *m*, H-3, 5) and 6.85 (1H, *m*, H-6) which were suggested as 1,2,4-trisubstituted benzene, broad singlet proton of hydroxyl group at δ 5.50 and singlet signal of one methoxyl group appeared at δ 3.88 ppm. The multiplet signals at δ 5.07 indicated the presence of methylene protons of terminal double bond on C-3′ (Figure 1), confirmed by ^{1}H-^{1}H COSY spectrum of the H-2′ and H-3′. By the analysis of 2D NMR data and comparison data with those in the literature, compound **3** was identified as eugenol [7].

Compound **4** ($C_{20}H_{24}O_4$, M^+ = 328) was obtained as a yellow gum, $[\alpha]_D^{27.5}$ = +7.8° (c = 0.32, $CHCl_3$). Its IR spectrum showed the presence of hydroxyl group at 3538, C=C of aromatic ring at 1608, and methylenedioxy group at 933 cm^{-1}. The ^{1}H NMR data demonstrated that **4** was a dibenzylbutane type of lignan. The proton signals at δ 6.73 (*d*, *J* = 7.9 Hz, H-5), 6.61 (*dd*, *J* = 8.2, 1.5 Hz, H-6) and 6.66 (*d*, *J* = 1.6 Hz, H-2) and three protons of aromatic ring at δ 6.83 (*d*, *J* = 7.9 Hz, H-5′), 6.62 (*d*, *J* = 1.5 Hz, H-2′) and 6.65 (*dd*, *J* = 8.2, 1.6 Hz, H-6′) were suggested that the aromatic rings each had a 1, 2, 4-trisubstitution pattern. The singlet signal at δ 5.92 ppm of two protons, broad singlet at δ 5.50 ppm of one proton and the singlet signal of three protons at δ 3.86 ppm indicated the presence of methylenedioxy, hydroxyl and methoxyl moieties in **4**, respectively. The correlation in the HMBC experiment indicated that the methylenedioxy, hydroxyl and methoxyl group were located at C3-C4, C-4′ and C-3′ (Figure 1), respectively. The signal at 1.74 (2H, *m*, H-8,8′), 2.25 (1H, *dd*, *J* = 13.6, 9.1 Hz, H-7′), 2.29 (1H, *dd*, *J* = 13.6, 5.0 Hz, H-7) and 2.72 (2H, *dd*, *J* =13.6, 5.0 Hz, H-7,7′) were suggested the presence of the butane with two methyl groups which resonated at δ 0.83 (3H, *d*, *J* = 6.6 Hz, H-9) and 0.85 (3H, *d*, *J* = 6.6 Hz, H-9′). By comparison spectroscopic data with those reported in the literature, compound **4** were suggested to be 2,3-dimethyl-1, 4-diaryl-butane or macelignan [8].

Compound **5** and **6** were obtained as colorless solids.The EIMS spectrometry showed molecular ion peaks at *m*/*z* 414 and 412 $[M]^+$ that correspond to the molecular

formula $C_{29}H_{50}O$ and $C_{29}H_{48}O$, respectively. Their IR spectrum exhibited the absorption band at 3396 cm^{-1} which is characteristic of O-H stretching. The absorption band at 1642 cm^{-1} is due to C=C of alkene groups. The ^1H NMR spectrum clearly showed that **5** and **6** were β-sitosterol and stigmasterol. The signal at δ 5.43 ppm (1H, *m*) was assigned as olefinic proton H-6 and the signal appeared at δ 3.52 ppm (1H, *m*) was assigned to H-3 connected to hydroxyl group for both β-sitosterol and stigmasterol. The signal at δ 5.14 (1H, *dd*, *J* = 15.2, 8.6 Hz) and 5.01 (1H, *dd*, *J* = 15.2, 8.6 Hz) were assigned to H-22 and H-23 of stigmasterol. The mixture of compound **5** and **6** was proved

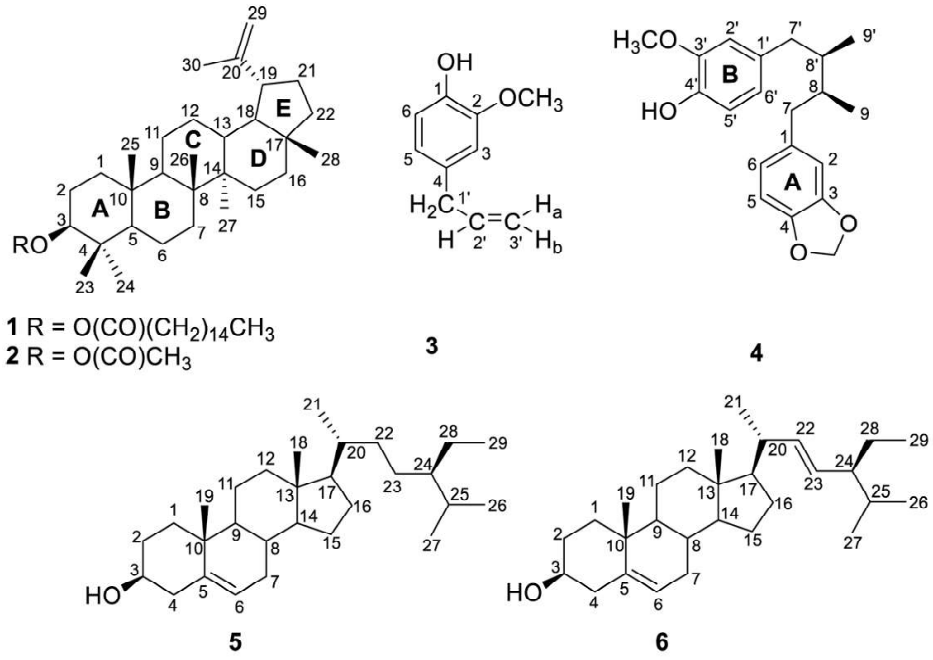

Figure 1. Structures of isolated compounds from *D. vagans*.

to contain β-sitosterol and stigmasterol by comparison of their ^1H NMR data with those previously reported in the literature [9].

3.2 Chemotaxonomic Significance

Compounds **1-6** were isolated from the twigs of *D. vagans*. Noteworthy, this is the first time that these compounds were isolated from this species. Twelve species of *Vernonia* genus were placed to *Decaneuropsis* genus which both genera are in the Asteraceae family. Lupeol palmitate (**1**) was previously isolated from *Vernonia westiniana* Less. [10], while lupeol acetate (**2**) was afforded from the leaves of *Vernonia auriculifera* Hiern. [11], *Vernonia cinerea* (L.) Less. [12], *Vernonia edverbengii* Gray. [13] and *V. westiniana* Less. [10]. Additionally, eugenol (**3**) was found in the leaf extract of *Vernonia arborea* Buch.-Ham. ex Buch.-Ham as analyzed by GC-MS [14]. The β-sitosterol (**5**) and stigmasterol (**6**) are found common in many plants and were previously reported the isolation from the bulbs of *Vernonia cotoneaster* (Willd. ex Spreng.) Less. [15]. Nevertheless, only macelignan (**4**) was isolated from the family Asteraceae for the first time. The isolation of eugenol (**3**)

was confirmed the occurrence of macelignan (**4**) in this species. Macelignan is a dibenzyl butane without 9(9′)oxygen which is produced by isoeugenol *via* phenolic oxidative coupling. While, eugenol and isoeugenol are produced from the same precursor, coniferyl acetate [16]. However, macelignan (**4**) has been formerly reported in the arils of *Myristica fragrans* Houtt. [17], the mace of *Myristica argentea* Warb. [8] and the bark of *Virola calophylla* (Spruce) Warb. [18].

4. CONCLUSION

The phytochemical of the twigs of *D. vagans* was investigated and resulted in the isolation of six known compounds. All compounds were identified from this plant for the first time and compound **4** has not been isolated from any genus of the Asteraceae. To the best of our knowledge, this is the report of chemical constituents from *Decaneuropsis* genus and may be used as foundation for further chemotaxonomic studies.

ACKNOWLEDGEMENTS

We are grateful to the Center of Excellence for Innovation in Chemistry (PERCH-CIC) for financial support and the Department of Chemistry Chiang Mai University for all facilities. This work was partially supported by Chiang Mai University.

REFERENCES

[1] Robinson H. and Skvarla J.J, *P. Biol. Soc. Wash.*, 2007; **120**: 359-366. DOI 10.2988/0006-324X(2007)120[359:SOTGAV]2.0.CO;2.

[2] Ma G.X., Feng W., Sun Z.H., Li P.F., Zhu N.L., Yang J.S., Xu X.D. and Wu H.F., *J. Carbohydr. Chem.*, 2016; **35**: 172-179. DOI 10.1080/07328303.2016.1170137.

[3] Iwagawa T., Omagari Y., Ueno C. and Hase T., *Rep. Fac. Sci. Kagoshima Univ.*, 1982; **15**: 63-68.

[4] Appleton R.A. and Enzell C.R., *Phytochemisty*, 1971; **10**: 447-449. DOI 10.1016/S0031-9422(00)94072-X.

[5] Wang K.W., *Nat. Prod. Res.*, 2007; **21**: 669-674. DOI 10.1080/14786410701371447.

[6] Prachayasittikul S., Saraban P., Cherdtrakulkiat R., Ruchirawat S. and Prachayasittikul V., *EXCLI J.*, 2010; **9**: 1-10.

[7] Locci E., Lai S., Piras A., Marongiu B. and Lai A., *Chem. Biodivers.*, 2004; **1**: 1354-1366. DOI 10.1002/cbdv.200490098.

[8] Filleur F., Pouget C., Allais D.P., Kaouadji M. and Chulia A.J., *Nat. Prod. Lett.*, 2002; **16**: 1-7. DOI 10.1080/1057563029001/4764.

[9] Pateh U.U., Haruna A.K., Garba M., Iliya I., Sule I.M., Abubakar M.S. and Ambi A.A., *Nigerian J. Pharm. Sci.*, 2009; **8**: 19-25.

[10] Rustaiyan A., Niknejad A., Danieli B., Palmisano G. and Jones S., *Fitoterapia*, 1977; **48**: 266-267.

[11] Kiplimo J.J., Koorbanally N.A. and Chenia H., *Afr. J. Pharm. Pharmacol.*, 2011; **5**: 1150-1156. DOI 10.5897/AJPP11.183.

[12] Misra T.N., Singh R.S., Srivastava R., Pandey H.S., Prasad C. and Singh S., *Planta Med.*, 1993; **59**: 458-460. DOI 10.1055/s-2006-959732.

[13] Dominguez X.A., Cano G., Sanchez H., Velazquez G., Ellmauerer E. and Jakupovic J., *J. Nat. Prod.*, 1986; **49**: 704-705. DOI 10.1021/np50046a030.

[14] Janakiraman K.S. and Chinnagounder S., *J. Pharm. Res.*, 2012; **5**: 2900-2905.

[15] dos Santos E.O., Meira M., do Vale A.E., David J.M., de Queiroz L.P. and David J.P., *Nat. Prod. Commun*., 2012; **7**: 781-783.

[16] Suzuki S. and Umezawa T., *J. Wood Sci*., 2007; **53**: 273-284. DOI 10.1007/s10086-007-0892-x.

[17] Woo S.W., Shin K.H., Wagner H. and Lotter H., *Phytochemistry*, 1987; **26**: 1542-1543. DOI 10.1016/S0031-9422(00)81858-0.

[18] Martinez J.C., Yoshida M. and Gottlieb O.R., *Phytochemistry*, 1990; **29**: 2655-2657. DOI 10.1016/0031-9422(90)85206-U.