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FLAVONOID *C*-GLUCOSIDES AND OTHER COMPOUNDS FROM AERIAL PARTS OF *DERRIS SCANDENS*

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Summary

Flavonoid *C*-glucosides and Other Compounds from Aerial Parts of *Derris scandens*

Six compounds were isolated and characterized from aerial parts of *Derris scandens*. Their structures were elucidated by spectroscopic techniques as heneicosan-1-ol (**1**), lupenone (**2**), behenic acid (**3**), rutin (**4**), 6-*C*-glucopyranosylquercertin (**5**), and 8-*C*-glucopyranosylquercertin (**6**). Except for rutin, other compounds were reported for the first time in the genus *Derris*.

Keywords: *Derris scandens, 6-C-glucopyranosylquercertin, 8-C-glucopyranosylquercertin, rutin.*

1. Introduction

Derris scandens (Roxb.) Benth. (Family Leguminosae) is distributed in Southeast Asia and Australia [1]. In India and Thailand, the stem was widely used in traditional medicine as an anti-tussive, diuretic, expectorant, anti-dysentery agent and for treatment of muscle pains, cough, and diarrhea [1],[2]. The powder and hydroalcoholic extract of *D. scandens* stem were recorded in the National List of Essential Medicines of Thailand for the treatment of muscle pain, low back pain, and knee osteoarthritis. *D. scandens* may be considered as an alternative for musculoskeletal pain reduction because of efficaciousness and safety [2]. Previous studies indicated the presence of coumarins, flavones, isoflavones, and their glycosides… as chemical constituents from *D. scandens* [1],[3]. To the best of our knowledge, there is no report on the chemical constituents

from this species in Vietnam. Here, we describe the isolation and structure elucidation of flavonoid *C*-glucosides and other compounds from aerial parts of *D. scandens*.

2. Material and methods

2.1. Plant material

The aerial parts of *Derris scandens* were collected by Mr. Le Van Son in the South of Vietnam in March 2021, from Binh Chau - Phuoc Buu Nature reserve, Xuyen Moc district, Ba Ria - Vung Tau province. The plant identification was performed by Mr. Nguyen Van Hieu (Department of Medicinal Plant Resources - National Institute of Medicinal Materials (NIMM) (mã số tiêu bản mẫu?). The aerial parts were dried in an oven at 40°C for 48 hours and shredded to 2 to 5 cm in size. The material was reserved in a nylon container in a cool and dried place for further studies.

2.2. General experimental procedures

Silica gel (Merck, Darmstadt, Germany, particle size 40 - 63 µm), D101 macroporous resin (Nankai Hecheng S&T, Tianjin china), Sephadex® LH-20 (GE Healthcare) were used for column chromatography. Thin-Layer Chromatography (TLC) was performed using pre-coated *silica gel* 60 F_{254} plates (Merck); spots were detected under UV 254 nm and/or by spraying with H_2SO_4 10% reagent in ethanol, followed by heating at 120°C for 1 - 2 min. Flavonoid *C*-glucosides were isolated by preparative HPLC Shimadzu LC20-AP with Supelco Analytical Discovery ® HS C_{18} (250 × 21,2 mm; 10 µm) column. ^{1}H- and ^{13}C-NMR were measured in $CDCl_3$ and DMSO-d_6 on a Bruker 600 NMR spectrometer (600 MHz for ^{1}H-NMR and 150 MHz for ^{13}C-NMR). Chemical shifts were expressed in δ (ppm) and tetramethylsilane (TMS) was used as an internal standard. Electrospray Ionization Mass Spectrometry (ESI-MS) spectra were recorded on an Agilent 1260 Series Single Quadrupole LC/MS Systems (Agilent, USA).

2.3. Extraction and isolation

The dried aerial parts (8 kg) of *D. scandens* were extracted with 70% aqueous ethanol three times under reflux. After filtration, solvents were removed under reduced pressure to obtain an ethanol extract. This extract was suspended in water and successively fractionated with dichloromethane and *n*-butanol. Solvents were evaporated in the vacuum condition to obtain the corresponding dichloromethane (DS.D, 207 g), *n*-butanol (DS.B, 252 g), and aqueous extract (DS.W, 660 g).

The dichloromethane extract (DS.D, 190 g) was initially chromatographed over a *silica gel* column using $CHCl_3$ and MeOH (100:0, 50:1, 30:1, 15:1, 5:1, 3:1, 1:1 and 0:100) to yield nine fractions (DS.D.I -DS.D.9). Fraction DS.D.II (9.2 g) was subjected to column chromatography over a *silica gel* column with a solvent mixture of *n*-hexane and ethyl acetate (50:1, 30:1, 15:1, 10:1, 5:1, 2:1) to yield seven subfractions (DS.D.II.1-DS.D.II.6). Subfraction DS.D.II.2 (765 mg) was chromatographed over *silica gel* column with a solvent mixture of *n*-hexane and ethyl acetate (100:1, 50:1, 15:1, 10:1) to obtain compound **1** (22 mg). Subfraction DS.D.II.3 (987 mg) was chromatographed over *silica gel* column with a solvent mixture of *n*-hexane and ethyl acetate (100:1, 50:1, 15:1, 10:1) and Sephadex LH-20 column with 100% acetone to yield compound **2** (14 mg). Fraction DS.D.IV (20.4 g) was purified by *silica gel* column with *n*-hexane and acetone (100:0, 100:1, 50:1, 30:1, 15:1, 5:1) to yield eight fractions (DS.D.IV.1 - DS.D.IV.8). Subfraction DS.D.IV.6 (1.5 g) was chromatographed over *silica gel* column with a solvent mixture of *n*-hexane and acetone (50:1, 30:1, 15:1, 10:1, 5:1) and Sephadex LH-20 column with 100% acetone to yield compound **3** (28 mg).

The *n*-butanol extract (DS.B, 230 g) was separated on D101 macroporous adsorption resin column washing with water and eluting with 10, 20, 30, 50, and 95% EtOH as elution reagents to afford six fractions (DS.B.I → DS.B.VI). Fraction DS.B.IV was concentrated (10% solids w/v) and then filtrated to afford a pale yellow powder (3.2 g). This precipitate (1.6 g) was twice chromatographed separately on Sephadex LH-20 columns (Sigma-Aldrich) with MeOH as the mobile phase to give compound **4** (96 mg). The filtrate was concentrated to obtain 22.6 g of residue. A part of this residue (3.5 g) was fractionated by column chromatography on Sephadex LH-20 using MeOH to yield six subfractions (A-F). Subfraction D (446 mg) was further purified by pre-HPLC with a solvent system of acetonitrile and 0.01% TFA in water (0-10': 15% ACN, 10-15': 15%-18% ACN, 15-50': 18% ACN). The flow rate was set at 6.0 mL/min and compounds were detected at wavelengths of 254 nm and 350 nm to obtain compounds **5** (5.4 mg) and **6** (80 mg).

Heneicosan-1-ol (1): White solid. ESI-MS: *m/z* 313.1 $[M+H]^+$. ^{1}H-NMR (600 MHz, $CDCl_3$): δ_H ppm 3.64 (2H, *t*, *J* = 6.6 Hz, H-1), 1.20 - 1.70 (38H, *m*, H-2 → H-20), 0.88 (3H, *t*, *J* = 7.2 Hz, H-21).

^{13}C-NMR (150 MHz, $CDCl_3$): δ_C ppm 14.1 (C-21), 31.8-22.7 (19 x CH_2, C-2 to C-20), 63.1 (C-1).

Lupenone (2): White needle crystals. ESI-MS: *m/z* 425.1 $[M+H]^+$. ^{1}H-NMR ($CDCl_3$, 600 MHz): δ_H ppm 4.69 (1H, *brd*, *J* = 2.5 Hz, H-29), 4.57 (1H, *m*, H-29), 2.48 (1H, *m*, H-19), 1.89 (2H, *m*, H-21), 1.68 (3H, *s*, H-30), 1.07 (6H, *s*, H-23 and H-24), 1.03 (3H, *s*, H-26), 0.96 (3H, *s*, H-25), 0.93 (3H, *s*, H-28), 0.80 (3H, s, H-27). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ_C ppm 218.2 (C-3), 150.9 (C-20), 109.4 (C-29), 55.0 (C-5), 49.8 (C-9), 48.3 (C-18), 48.0 (C-19), 47.3 (C-4), 43.0 (C-14), 42.9 (C-17), 40.8 (C-8), 40.0 (C-22), 39.6 (C-1), 38.2 (C-13), 36.9 (C-10), 35.5 (C-16), 34.2 (C-2), 33.6 (C-7), 29.8 (C-21), 27.4 (C-15), 26.7 (C-23), 25.2 (C-12), 21.5 (C-11), 21.0 (C-24), 19.7 (C-6), 19.3 (C-30), 18.0 (C-28), 16.0 (C-25), 15.8 (C-26), 14.5 (C-27).

Behenic acid (3): Colorless waxy semisolid. ESI-MS: *m/z* 341.2 $[M+H]^+$. ^{1}H-NMR ($CDCl_3$, 600 MHz): δ_H ppm 2.34 (2H, *t*, *J* = 7.2 Hz, H-2), 1.63 (2H, *quin*, *J* = 7.2 Hz, H-3), 1.20 - 1.35 (36H, *brs*, H-4 → H-21), 0.88 (3H, *t*, *J* = 7.2 Hz, H-22). ^{13}C-NMR (150 MHz, $CDCl_3$): δ_C ppm 178.7 (COOH), 33.8 (C-2), 22.7-29.7 (C-3 → C-19, C-21), 32.0 (C-20), 14.1(C-22).

Rutin (4): Yellow amorphous powder. ^{1}H-NMR (600 MHz, DMSO-d_6): δ_H ppm 12.59 (1H, *s*, OH-5), 6.19 (1H, *d*, *J* = 2.4 Hz, H-6), 6.38 (1H, *d*, *J* = 2.4 Hz, H-8), 7.53 (2H, *m*, H-2′ and H-6′), 6.84 (1H, *d*, *J* = 8.4 Hz, H-5′), 5.34 (1H, *d*, *J* = 7.8 Hz, H-1″), 3.7 (1H, *d*, *J* = 10.0 Hz, H-6″), 4.38 (1H, *d*, *J* = 1.2 Hz, H-1‴), 0.99 (3H, *d*, *J* = 6.6 Hz, H-6‴). ^{13}C-NMR (150 MHz, DMSO-d_6): δ_C ppm 156.6 (C-2), 133.3 (C-3), 177.4 (C-4), 161.2 (C-5), 98.7 (C-6), 164.1 (C-7), 93.6 (C-8), 156.4 (C-9), 104.0 (C-10), 121.2 (C-1′), 116.3 (C-2′), 144.4 (C-3′), 148.4 (C-4′), 115.2 (C-5′), 121.6 (C-6′), 101.2 (C-1″), 74.1 (C-2″), 76.5 (C-3″), 70.4 (C-4″), 75.9 (C-5″), 68.3 (C-6″), 100.8 (C-1‴), 70.6 (C-2‴), 71.9 (C-3‴), 74.1 (C-4‴), 70.0 (C-5‴), 17.7 (C-6‴).

6-*C*-Glucopyranosylquercertin (5): Yellow amorphous powder. ESI-MS: *m/z* 367.0 $[M-120+Na]^+$. ^{1}H-NMR (600 MHz, DMSO-d_6): δ_H ppm 13.07 (1H, *s*, OH-5), 6.45 (1H, *s*, H-8), 7.67 (1H, *d*, *J* = 2.4 Hz, H-2′), 6.88 (1H, *d*, *J* = 8.4 Hz, H-5′), 7.55 (1H, *dd*, *J* = 2.4, 8.4 Hz, H-6′), 4.60 (1H, *d*, *J* = 9.6 Hz, H-1″), 4.06 (1H, *m*, H-2″), 3.0-3.75 (5H, *m*, H-3″ → H-6″). ^{13}C-NMR (150 MHz, DMSO-d_6): δ 146.6 (C-2), 136.6 (C-3), 176.0 (C-4), 159.8 (C-5), 108.1 (C-6), 163.1 (C-7), 93.0 (C-8), 155.0 (C-9), 102.7 (C-10), 121.9 (C-1′), 115.0 (C-2′), 145.1 (C-3′), 147.7 (C-4′), 115.6 (C-5′), 120.0 (C-6′), 73.1 (C-1″), 70.2 (C-2″), 79.0 (C-3″), 70.6 (C-4″), 81.6 (C-5″), 61.5 (C-6″).

8-*C*-Glucopyranosylquercertin (6): Yellow amorphous powder. ESI-MS: *m/z* 465.0 $[M+H]^+$. ^{1}H-NMR (600 MHz, DMSO-d_6): δ_H ppm 12.68 (1H, *s*, OH-5), 6.26 (1H, *s*, H-6), 7.86 (1H, *d*, *J* = 1.8 Hz, H-2′), 6.84 (1H, *d*, *J* = 8.4 Hz, H-5′), 7.65 (1H, *dd*, *J* = 1.8, 8.4 Hz, H-6′), 4.67 (1H, *d*, *J* = 10.2 Hz, H-1″), 3.86 (1H, *m*, H-2″), 3.20~3.40 (3H, *m*, H-3″ → H-5″), 3.88 (1H, *m*, H-6″a), 3.58 (1H, *m*, H-6″b). ^{13}C-NMR (150 MHz, DMSO-d_6): δ_C ppm 147.0 (C-2), 135.5 (C-3), 176.0 (C-4), 159.6 (C-5), 97.5 (C-6), 162.2 (C-7), 104.0 (C-8), 154.8 (C-9), 103.4 (C-10), 122.3 (C-1′), 115.9 (C-2′), 145.0 (C-3′), 147.6 (C-4′), 115.4 (C-5′), 120.3 (C-6′), 73.4 (C-1″), 70.4 (C-2″), 78.8 (C-3″), 70.6 (C-4″), 81.9 (C-5″), 61.6 (C-6″).

3. Results and discussions

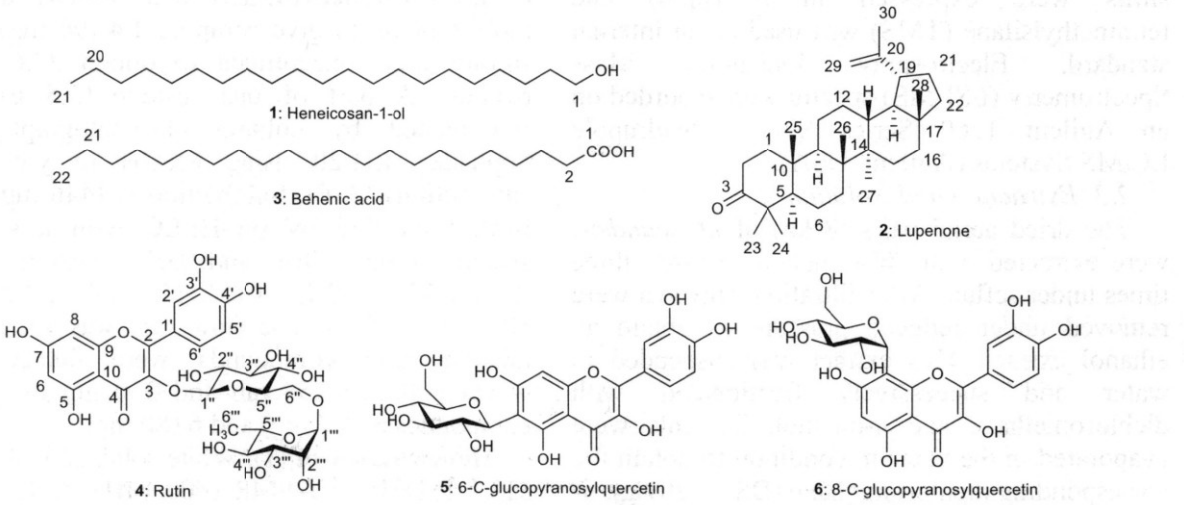


Fig. 1. Structures of six compounds (**1-6**) from *D. scandens*

Compound **1** was obtained as a white solid. Its molecular formula was predicted as $C_{21}H_{44}O$ by ESI-MS showing a pseudomolecular ion at *m/z* 313.1 $[M+H]^+$. The ^{1}H-NMR spectrum displayed a triplet signal at δ_H 3.64 (2H, *t*, *J* = 6.6 Hz, H-1) assignable to a hydroxymethylene group. A triplet signal at δ_H 0.88 (3H, *t*, *J* = 7.2 Hz, H-22) was attributed to the terminal methyl protons. The ^{13}C-NMR and DEPT spectra of **1** displayed signals for the hydroxymethylene carbon at δ_C 63.21 (C-1), methylene carbons from δ_C 32.8 to 22.7, and the methyl carbon at δ_C 14.13 (C-31). Based on the 1D-NMR spectrum analysis and comparison with those previously reported in literature [4], compound **1** was established as heneicosan-1-ol.

Compound **2** was obtained as white needle crystals. The ESI-MS of **2** showed a pseudomolecular ion $[M+H]^+$ at *m/z* 425.1 consistent with a molecular formula of $C_{30}H_{48}O$. The ^{1}H-NMR spectrum revealed the presence of seven singlet signals at δ_H 1.68 (3H, *s*, H-30), 1.07 (6H, *s*), 1.03 (3H, *s*), 0.96 (3H, *s*), 0.93 (3H, *s*) and 0.80 (3H, *s*) for methyl groups. A multiplet of one proton at δ_H 2.48 ascribable to H_β-19β is characteristic of lupenone. A pair of broad singlets at δ_H 4.69 (1H, *brd*, *J* = 2.5 Hz, H-29), 4.57 (1H, *m*, H-29) was indicative of olefinic protons. In the ^{13}C-NMR and DEPT spectra, the key signals included a carbonyl group at δ_C 178.7 (COOH), 218.2 (C-3) and an exomethylene group at δ_C 109.4 (C-29) and 15.9 (C-20). The structural assignment of **2** was further substantiated by the ^{13}C-NMR experiments which showed seven methyl groups at δ_C 26.7 (C-23), 21.0 (C-24), 19.3 (C-30), 18.0 (C-28), 16.0 (C-25), 15.8 (C-26), and 14.5 (C-27)]; ten methylene, five methine, and five quaternary carbons were assigned with the aid of DEPT experiment. These assignments were in good agreement with the structure of lupenone [5],[6],[7].

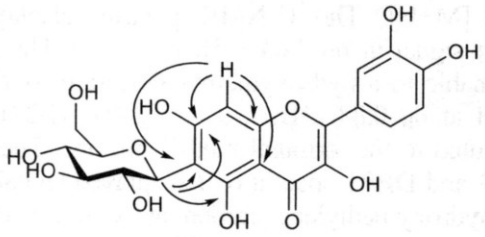
Compound **3** was obtained as colorless waxy semisolid. Its molecular formula $C_{22}H_{44}O_2$ was predicted by ESI-MS with a pseudo molecular ion peak at *m/z* 341.2 $[M+H]^+$. The ^{1}H-NMR spectrum showed proton signals at δ_H 2.34 (2H, *t*, *J* = 7.2 Hz, H-2), 1.63 (2H, *quin*, *J* = 7.2 Hz, H-3), 1.20 - 1.35 (36H, *brs*, H-4~21) and signal of terminal methyl protons at δ_H 0.88 (3H, *t*, *J* = 7.2 Hz, H-22). In the ^{13}C-NMR and DEPT spectra, the key signals included a carbonyl group at δ_C 178.7 (COOH) and the terminal methyl group at δ_C 14.1 (C-22). Compound **3** was identified as behenic acid by comparing with the spectral data in the literature [8].

Compound **4** was also obtained as a yellow amorphous powder. The ^{1}H-NMR spectrum of compound **4** showed two doublets at δ_H 6.19 (1H, *d*, *J* = 2.4 Hz, H-6) and 6.38 (1H, *d*, *J* = 2.4 Hz, H-8) consistent with the *meta*-coupled protons H-6 and H-8 on the A-ring of a flavonoid, whereas the B-ring protons are characterized by the ABX system at δ_H 7.53 (2H, *m*, H-2′ and H-6′), 6.84 (1H, *d*, *J* = 8.4 Hz, H-5′) suggesting the present of a 3′,4′-disubstituted B-ring. The signals for the anomeric protons of the glucopyranosyl and rhamnopyranosylsyl units appeared at δ_H 5.34 (1H, *d*, J = 7.8 Hz, H-1″) and 4.38 (1H, *d*, J = 1.2 Hz, H-1‴), respectively. Additionally, the methyl protons of rhamnose sugar appeared at δ_H 0.99 (3H, *d*, *J* = 6.6 Hz, H-6‴). In the HMBC spectrum, the Rha H-1‴ (δ_H 4.38) correlated with the Glc C-6″ (δ_C 67.0) indicating a rutinosyl moiety. Finally, the Glc H-1″-hydrogen atom (δ_H 5.34) correlated with C-3 (δ_C 133.3) of the flavonoid unit in the HMBC spectrum, indicating *O*-rutinosyl group at C-3. The analysis of the one- and two-dimensional NMR spectra of **4** and comparison with literature data led to the assignment of compound **4** as quercetin-3-*O*-rutinoside (rutin) [9],[10].

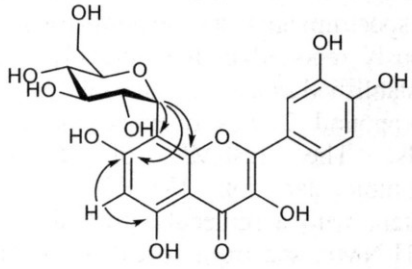
Compound **5** was also obtained as a yellow amorphous powder. The molecular formula of compound **5** was predicted as $C_{21}H_{20}O_{12}$ by ESI-MS showing an ion at *m/z* 367.0 $[M-120+Na]^+$. The ^{1}H-NMR spectrum of compound **5** showed a singlet signal at δ_H 6.38 (1H, *d*, *J* = 2.4 Hz, H-8) consistent with the proton H-8 on the A-ring of a flavonoid, whereas the B-ring protons were characterized by the ABX system at δ_H 7.67 (1H, *d*, *J* = 2.4 Hz, H-2′), 6.84 (1H, *d*, *J* = 8.4 Hz, H-5′), 7.55 (1H, dd, *J* = 1.8, 8.4 Hz, H-6′) suggesting a 3′,4′-disubstituted B-ring. The signals for the proton of the glucosyl unit appeared at δ_H 4.60 (1H, *d*, *J* = 9.6 Hz, H-1″), 4.06 (1H, *m*, H-2″), 3.10 → 3.75 (5H, *m*, H-3″ → H-6″). In the ^{13}C-NMR spectrum, the signals for the carbon of the glucopyranosyl unit appeared at δ_C 73.1 (C-1″), 70.2 (C-2″), 79,0 (C-3″), 70,6 (C-4″), 81,6 (C-5″) and 61.5 (C-6″). In HSQC spectrum, the signal of Glc H-1″ (δ_H 4.60) correlated with the signal of Glc C-1″ (δ_C 73.1), indicating that the glucose moiety was attached directly to the flavonoid nucleus by a carbon-carbon bond. In the HMBC spectrum, the signal of H-8 (δ_H 6.38) correlated with signals of 176.0 (C-4), 108.1 (C-6), 163.1 (C-7), 155.0 (C-9), 102.7 (C-10) and C-1″ (δ_C 73.1). Additionally, the signal of Glc H-1″ (δ_H 4.60) correlated with signals of C-5 (δ_C 159.8), C-6 (δ_C 108.1) and C-7 (δ_C 163.1) (Fig. 2). Analysis of the one- and two-dimensional NMR spectra of **5** and comparison with the literature led to the

assignment of compound **5** as 6-*C*-glucopyranosylquercetin [11].

Compound **6** was also obtained as a yellow amorphous powder. Its molecular formula was predicted as $C_{21}H_{20}O_{12}$ by ESI-MS, showing an ion peak at *m/z* 465.0 $[M+H]^+$. The ^{1}H-NMR spectrum of compound **6** showed a singlet at δ_H 6.26 (1H, *d*, *J* = 2.4 Hz, H-6) consistent with the proton H-6 on the A-ring of a flavonoid, whereas the B-ring protons are characterized by the ABX system at δ_H 7.86 (1H, *d*, *J* = 1.8 Hz, H-2′), 6.84 (1H, *d*, *J* = 8.4 Hz, H-5′), 7.65 (1H, *dd*, *J* = 1.8, 8.4 Hz, H-6′) suggesting a 3′,4′-disubstituted B-ring. The signals for protons of a glucosyl unit appeared at δ_H 4.67 (1H, *d*, *J* = 10,2 Hz, H-1″), 3.86 (1H, *m*, H-2″), 3.20-3.40 (3H, *m*, H-3″→5″), 3.88 (1H, *m*, H-6″a), 3.58 (1H, *m*, H-6″b). In the ^{13}C-NMR spectrum signals for the carbons of the glucopyranosyl unit appeared at 73.4 (C-1″), 70.4 (C-2″), 78.8 (C-3″), 70.6 (C-4″), 81.9 (C-5″), and 61.6 (C-6″). In HSQC spectrum, the signal of Glc H-1″ (δ_H 4.67) correlated with the signal of Glc C-1″ (δ_C 73.4), indicating that the glucose moiety was attached directly to the flavonoid aglycon by a carbon-carbon bond. In the HMBC spectrum, the signal of H-6 (δ_H 6.26) correlated with signals of 176.0 (C-4), 159.6 (C-5), 162.2 (C-7), 103.4 (C-10) and C-1″ (δ_C 73.1). Additionally, the signal of Glc H-1″ (δ_H 4.67) correlated with signals of 162.2 (C-7), 104.0 (C-8) and 154.8 (C-9) (Fig. 2). Analysis of the one- and two-dimensional NMR spectra of **6** led to the assignment of compound **6** as 8-*C*-glucopyranosylquercetin. In 2019, compound **6** was first identified from an enzymatic reaction with TcCGT1 (*C*-glycosyltransferase) [12]. Our study is the first report about the isolation of **6** in nature.



5



6

Fig. 2. Key HMBC correlation of **5** and **6**

4. Conclusion

Six compounds (**1-6**) were isolated from aerial parts of *Derris scandens*. Their chemical structures were identified as heneicosan-1-ol (**1**), lupenone (**2**), behenic acid (**3**), rutin (**4**), 6-*C*-glucopyranosylquercertin (**5**), and 8-*C*-glucopyranosylquercertin (**6**). Rutin was reported for the first time in the *Derris* genus in 2020 by Supun Mohotti et al. [13]. Five compounds (**1-3**, **5**, and **6**) were found for the first time in the genus *Derris*.

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