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POLYPHENOLIC COMPOUNDS FROM THE LEAVES OF *SCHINUS TEREBINTHIFOLIUS* RADDI

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من اوراق نبات شينوس تربنتيفوليوس تم فصل والتعرف على المركبات الآتية: ٥ أ كافيويل حامض الكوينك (١)، ٥ أ كوماروبل حامض الكوينك (٢)، ميريسيتين٣ أ الفا رامنوبيرانوزيل (١←٦) بيتا جالاكتوبيرانوزيد (٣) ، ميريسيتين٣ أ جلوكيرونيد (٤) ، ميريسيتين ٣ أ جالاكتوبيرانوزيد (٥)، ١و٦ ثنائى جالويل بيتا جلوكوز (٦) ، كاتيكين (٧) وهذه المركبات تفصل لأول مرة من النبات. كذلك تم فحص محتوى حامض التانيك بإستخدام كروماتوجرافيا السائل تحت ضغط عال.

*Two quinic acid esters, 5-O-caffeoylquinic acid (**1**) and 5-O-coumaroylquinic acid (**2**); three myricetin glycosides, myricetin 3-O-α-L-rhamnopyranosyl(1‴→6″)β-D-galactopyranoside (**3**), myricetin 3-O-β-D-glucuronide (**4**), and myricetin 3-O-β-D-galactopyranoside (**5**); 1,6-digalloyl-β-D-glucose (**6**); and (+)-catechin (**7**) were isolated and identified for the first time from the leaves of Schinus terebinthifolius Raddi. Furthermore, investigation of tannic acid content was carried out by HPLC.*

INTRODUCTION

The family Anacardiaceae comprises about 600 species belonging to 70 genera. The plants of this family are mainly tropical trees and shrubs used for dyeing and tanning. The genus *Schinus* is a member of this family, which includes 30 species[1]. The tree of *Schinus terebinthifolius* Raddi (pepper tree) is evergreen, has leathery imparipinnate leaves, with an abudance of small flowers formed in panicles. The fruits are small bright-red drupes[2]. The bark of *S. terebinthifolius* Raddi is used for dressing leather and a dye is also extracted from it[2]. The extract of the stem bark is used as an anti-inflammatory and wound-healing agent[3]. The leaves and stem bark are used as tonic, to treat wounds, and urinary and respiratory tract

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infections. They have antiseptic, anti-inflammatory, balsamic, haemostatic, and antioxidant activities[4]. The essential oil of the plant is used to treat respiratory problems, mycosis, and candidal infections (topical use); its activity is attributed to the presence of high concentrations of monoterpenes in the plant[4]. Ethanolic extracts from the leaves, stem bark, and fruits exhibited antimicrobial activity[4-6]. Pentagalloylglucose isolated from the aerial parts of this plant has been reported to exhibit inhibitory activity against xanthine oxidase[7]. Polyphenols purified from the leaves of the plant induced anti-proliferative effect[8]. Triterpenoids present in the berries have been shown to act as specific competitive inhibitors of secreted phospholipase-A_2[9].

Leaves and bark of the pepper tree contain tannins and essential oil[10]. The results of the chemical analysis of the stem bark showed the presence of catechin, saponins, terpenes, and flavonoids[3]. Phytochemical study of the drupes led to the isolation of apigenin, naringin, ellagic, syringic acid[5], biflavonoids, gallic acid[11], penta galloylglucose[7], *n*-alkyl-phenols[12], and cardanol[13].

This paper deals with the isolation and identification of seven polyphenolic compounds including, 5-*O*-caffeoylquinic acid (**1**), 5-*O*-coumaroylquinic acid (**2**), myricetin 3-*O*-α-L-rhamnopyranosyl(1'''→6'')β-D-galactopyranoside (**3**), myricetin 3-*O*-β-D-glucuronide (**4**), myricetin 3-*O*-β-D-galactopyranoside (**5**), 1,6-digalloyl-β-D-glucose (**6**), and (+)-catechin (**7**) from the leaves of *S. terebinthifolius* Raddi. Moreover, investigation of tannic acid content was carried out by normal-phase HPLC.

EXPERIMENTAL

General procedures

NMR experiments were recorded in CD_3OD and DMSO-d_6 using a Varian Unity Inova AS600NB spectrometer (600 MHz for ^1H NMR and 150 MHz for ^{13}C NMR). UV spectra were measured with a JASCO V-530 UV–VIS spectrophotometer (Jasco, Tokyo, Japan). The IR (KBr) spectra were taken on a JASCO FT/IR-410 spectrophotometer. Column chromatography was carried out on Toyopearl HW-40 (coarse grade; Tosoh Company, Tokyo, Japan), Diaion HP-20 (Mitsubishi Chemical Industries, Tokyo, Japan) and MCI-gel CHP-20P (75–150 μm, Mitsubishi Kasei Company, Tokyo, Japan). Preparative TLC was performed on Kieselgel 60 F_{254} plates (layer thickness of 0.5 mm; Merck, Darmstadt, Germany), while analytical TLC was conducted on precoated aluminium sheets of silica gel 60 GF_{254} (Merck, Darmstadt, Germany) using $CHCl_3$-MeOH-H_2O (65:30:5). The spots were detected by UV irradiation (254 and 366 nm) followed by spraying with 10% H_2SO_4 reagent or 5% $AlCl_3$. Authentic samples of chlorogenic acid, tannic acid and 1,2,3,4,6-pentagalloyl-β-D-glucose were obtained from Division of

Pharmaceutical Sciences, Okayama University Graduate School of Medicine, Dentistry and Pharmaceutical Sciences, Tsushima, Okayama 700-8530, Japan.

Plant material

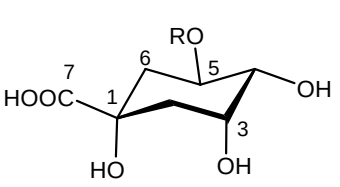
The leaves of *Schinus terebinthifolius* Raddi were collected during the flowering stage in July 2006 from the Experimental Station of Medicinal Plants, Faculty of Agriculture, Assiut University, Assiut, Egypt. The plant was identified by Prof. Dr. Naeem El-Keltawy, Prof. of Horticulture, Faculty of Agriculture, Assiut University. A voucher sample has been deposited in the Herbarium of Pharmacognosy Department, Faculty of Pharmacy, Assiut University, Assiut, Egypt.

Extraction and isolation

Air-dried powdered leaves of *S. terebinthifolius* Raddi (2.0 kg) were extracted with 70% aqueous acetone (3×6 L) and the combined extracts filtered and concentrated. The extract was suspended in H_2O (1 L) and successively partitioned with Et_2O (3×1 L), EtOAc (3×1 L), and *n*-BuOH saturated with H_2O (3×1 L). Each phase was concentrated under reduced pressure to give the corresponding soluble fraction (17.1 g), (114.7 g) and (73.0 g), respectively, in addition to 14.5 g as water soluble residue.

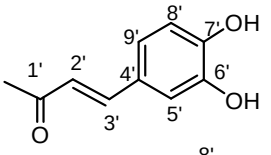
About 63.0 g of the *n*-BuOH fraction was applied to a column of Diaion HP-20 and eluted successively with H_2O, 20% MeOH, 40% MeOH, 60% MeOH and 100% MeOH to yield 5 fractions, B-I (24.0 g), B-II (4.5 g), B-III (10.4 g), B-IV (17.9 g), and B-V (4.0 g), respectively. About 2.3 g of fraction B-II was chromatographed over Toyopearl HW-40 (coarse grade) column (40 × 2.2 cm) and eluted with MeOH-H_2O gradient to yield 5 fractions: B-II-1 (2:8, 300.0 mg), B-II-2 (3:7, 137.9 mg), B-II-3 (4:6, 36.8 mg), B-II-4 (5:5, 102.7 mg), and B-II-5 (MeOH, 1.6 g). Fraction B-II-2 was purified on MCI-gel CHP-20P column (48 × 1.1 cm) using MeOH-H_2O (1:4) and MeOH-H_2O (3:7) as eluents to afford compounds **1** (37.0 mg) and **2** (27.0 mg), respectively. Fraction B-II-3 was subjected to preparative TLC to yield compounds **3** (8.4 mg) and **7** (9.5 mg), respectively. Fraction B-II-4 was purified on MCI-gel CHP-20P column and eluted with MeOH-H_2O (3:7) to yield compound **6** (3 mg) followed by MeOH-H_2O (2:3) to yield compounds **4** (18.3 mg) and **5** (8.0 mg).

Compound 1: Yellowish brown amorphous powder; R_f= 0.17; IR ν_{max} (KBr): 3375, 1706, 1677, 1627, 1595, 1508, 1433 cm^{-1}; ^1H NMR (CD_3OD, 600 MHz): δ 2.10~2.25 (4H, m, H_2-2/6), 3.77 (1H, dd, J= 9.0, 3.6 Hz, H-4), 4.21 (1H, m, H-3), 5.38 (1H, ddd, J= 13.8, 9.0, 4.2 Hz, H-5), 6.30 (1H, d, J= 16.2 Hz, H-2′), 6.82 (1H, d, J= 8.4 Hz, H-8′), 6.99 (1H, dd, J= 8.4, 2.4 Hz, H-9′), 7.09 (1H, d, J= 2.4 Hz, H-5′), 7.60 (1H, d, J= 16.2 Hz, H-3′); ^{13}C NMR (CD_3OD, 150 MHz):

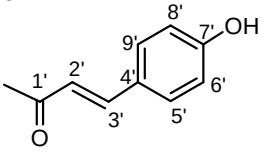


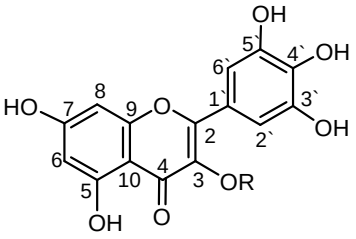
1 : R = Caffeoyl
2 : R = *p*-Coumaroyl

Caffeoyl =



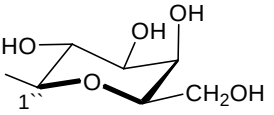
p-Coumaroyl =



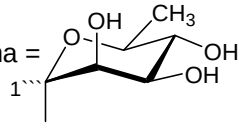


3 : R = Gal (6''→1''') Rha
4 : R = GlcA
5 : R = Gal

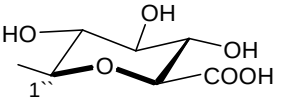
Gal =

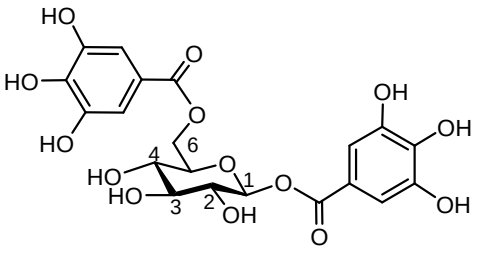


Rha =



GlcA =





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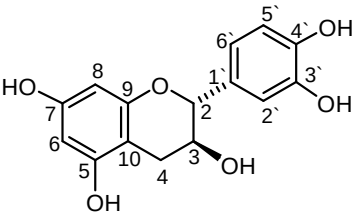

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Structures of compounds **1**–**7**.

δ 37.1 (C-2), 37.7 (C-6), 70.2 (C-3), 70.8 (C-5), 72.4 (C-4), 75.0 (C-1), 114.1 (C-2′/5′), 115.3 (C-8′), 121.8 (C-9′), 126.6 (C-4′), 145.6 (C-6′), 145.9 (C-3′), 148.4 (C-7′), 167.5 (C-1′), 175.9 (C-7).

Compound 2: Yellowish brown amorphous powder; R_f= 0.28; IR ν_{max} (KBr): 3400, 1706, 1682, 1631, 1596, 1504, 1433 cm^{-1}; ^{1}H NMR (DMSO-d_6, 600 MHz): δ 1.79~1.98 (4H, m, H_2-2/6), 3.56 (1H, m, H-4), 3.93 (1H,

m, H-3), 5.08 (1H, m, H-5), 6.27 (1H, d, J= 16.2 Hz, H-2′), 6.79 (2H, d, J= 8.4 Hz, H-6′/8′), 7.49 (1H, d, J= 16.2 Hz, H-3′), 7.52 (2H, d, J= 8.4 Hz, H-5′/9′); ^{13}C NMR (DMSO-*d*$_6$, 150 MHz): δ 41.8 (C-2), 42.6 (C-6), 73.6 (C-4), 75.9 (C-3), 76.3 (C-5), 78.9 (C-1), 119.9 (C-2′), 121.2 (C-6′/8′), 130.6 (C-4′), 135.7 (C-5′/9′), 149.9 (C-3′), 165.2 (C-7′), 171.2 (C-1′), 180.3 (C-7).

Compound 3: Yellowish brown amorphous powder; R_f= 0.32; UV (MeOH) λ_{max}: 258, 301 sh, 363; + NaOMe: 268, 322, 408; + $AlCl_3$: 270, 310 sh, 437; + $AlCl_3$/HCl: 272, 307, 415; + NaOAc: 270, 321, 408; + NaOAc/H_3BO_3: 258, 386 nm. ^{1}H NMR (CD_3OD, 600 MHz): δ 1.27 (3H, d, J= 6.6 Hz, H-6‴), 3.48 (1H, dd, J= 10.2, 7.2 Hz, H-6″b), 3.80 (1H, dd, J=10.2, 6.0 Hz, H-6″a), 3.54~3.90 (m, other sugar protons), 4.58 (1H, d, J= 1.8 Hz, H-1‴), 5.10 (1H, d, J= 7.8 Hz, H-1″), 6.21 (1H, d, J= 1.8 Hz, H-6), 6.40 (1H, d, J= 1.8 Hz, H-8), 7.45 (2H, s, H-2′/H-6′); ^{13}C NMR (CD_3OD, 150 MHz): δ 18.0 (C-6‴), 67.4 (C-6″), 69.7 (C-5‴), 70.2 (C-4″), 72.1 (C-3″), 72.3 (C-3‴), 73.2 (C-2″), 73.9 (C-4‴), 75.2 (C-2‴), 75.3 (C-5″), 95.4 (C-8), 100.8 (C-6), 102.0 (C-1‴), 104.8 (C-10), 106.4 (C-1″), 110.1 (C-2′/6′), 121.6 (C-1′), 136.0 (C-3), 138.3 (C-4′), 146.4 (C-3′/5′), 158.5 (C-2), 158.6 (C-9), 162.8 (C-5), 168.7 (C-7), 179.0 (C-4).

Compound 4: Yellow amorphous powder; R_f= 0.14; UV (MeOH) λ_{max}: 259, 302 sh, 365; + NaOMe: 269, 324, 410; + $AlCl_3$: 270, 308 sh, 430; + $AlCl_3$/HCl: 272, 307, 408; + NaOAc: 270, 326, 400; + NaOAc/H_3BO_3: 259, 380 nm. ^{1}H NMR (DMSO-*d*$_6$, 600 MHz): δ 3.24~3.42 (m, sugar protons), 3.54 (1H, d, J= 10.2 Hz, H-5″), 5.49 (1H, d, J= 7.8 Hz, H-1″), 6.19 (1H, d, J= 1.8 Hz, H-6), 6.37 (1H, d, J= 1.8 Hz, H-8), 7.19 (2H, s, H-2′/6′); ^{13}C NMR (DMSO-*d*$_6$, 150 MHz): δ 71.4 (C-4″), 73.8 (C-2″), 76.1 (C-5″), 76.2 (C-3″), 93.6 (C-8), 98.9 (C-6), 101.3 (C-10), 104.0 (C-1″), 108.7 (C-2′/6′), 119.9 (C-1′), 133.5 (C-3), 137.0 (C-4′), 145.6 (C-3′/5′), 156.3 (C-9), 156.4 (C-2), 161.4 (C-5), 164.4 (C-7), 170.0 (C-6″), 177.3 (C-4).

Compound 5: Yellow amorphous powder; R_f= 0.41; UV (MeOH) λ_{max}: 260, 300 sh, 363; + NaOMe: 270, 322, 408; + $AlCl_3$: 272, 308 sh, 437; + $AlCl_3$/HCl: 274, 307, 415; + NaOAc: 272, 322, 408; + NaOAc/H_3BO_3: 260, 386 nm. ^{1}H NMR (DMSO-*d*$_6$, 600 MHz): δ 3.27~3.63 (m, sugar protons), 5.30 (1H, d, J= 7.8 Hz, H-1″), 6.11 (1H, d, J= 1.8 Hz, H-6), 6.29 (1H, d, J= 1.8 Hz, H-8), 7.19 (2H, s, H-2′/H-6′); ^{13}C NMR (DMSO-*d*$_6$, 150 MHz): δ 60.2 (C-6″), 68.1 (C-4″), 71.4 (C-2″), 73.5 (C-3″), 76.1 (C-5″), 93.7 (C-8), 99.2 (C-6), 102.4 (C-1″), 103.5 (C-10), 108.7 (C-2′/6′), 120.0 (C-1′), 133.8 (C-3), 137.1 (C-4′), 145.6 (C-3′/5′), 156.1 (C-2), 156.5 (C-9), 161.3 (C-5), 165.6 (C-7), 177.3 (C-4).

Compound 6: White amorphous powder; R_f= 0.3; ^{1}H NMR (CD_3OD, 600 MHz): δ 3.55~3.75 (4H, m, H-2′,3′,4′,5′), 4.44 (1H, dd, J= 12.0, 5.4 Hz, H-6′b), 4.59 (1H, dd, J= 12.0, 1.8 Hz, H-6′a), 5.73 (1H, d, J= 7.8 Hz, H-1′), 7.12, 7.17 (each 2H, s, galloyl-H); ^{13}C NMR (CD_3OD, 150 MHz): δ 63.3 (C-6′), 70.0 (C-4′), 72.9 (C-2′), 75.3 (C-3′), 76.9 (C-5′), 94.8 (C-1′), 109.0, 109.4 (galloyl C-2/6), 119.9, 120.2 (galloyl C-1), 139.2, 139.5 (galloyl C-4), 145.3 (galloyl C-3/5), 165.8, 167.1 (galloyl-CO).

Compound 7: White amorphous powder; R_f= 0.74; ^{1}H NMR (CD_3OD, 600 MHz): δ 2.55 (1H, dd, J= 16.2, 7.8 Hz, H-4b), 2.89 (1H, dd, J= 16.2, 5.4 Hz, H-4a), 4.02 (1H, ddd, J= 7.8, 7.2, 5.4 Hz, H-3), 4.60 (1H, d, J= 7.2 Hz, H-2), 5.90 (1H, d, J= 1.8 Hz, H-6), 5.97 (1H, d, J= 1.8 Hz, H-8), 6.75 (1H, dd, J= 8.4, 2.4 Hz, H-6′), 6.80 (1H, d, J= 8.4 Hz, H-5′), 6.88 (1H, d, J= 2.4 Hz, H-2′).

Determination of the tannic acid content

Chromatographic equipment and conditions

Normal-phase HPLC was conducted on a YMC-Pack SIL A-003 column (250 mm × 4.6 mm i.d.; YMC, Kyoto, Japan) developed with *n*-hexane-MeOH-THF-formic acid 60:45:15:1 containing oxalic acid 500 mg/1.2 L (flow rate, 1.5 m L/min; UV detection, 280 nm) at room temperature.

Sample preparation

One milligram each of EtOAc and *n*-BuOH-soluble fraction as well as a reference sample of pentagalloyl-glucose (R_t= 6.45 min) was dissolved in 1 mL MeOH. Aliquots (2 μL) of each solution were subjected to HPLC and the areas under the peaks were recorded.

RESULTS AND DISCUSSION

Seventy percent aqueous acetone extract obtained from the leaves of *S. terebinthifolius* Raddi was suspended in H_2O and partitioned with Et_2O, EtOAc, and *n*-BuOH. The *n*-BuOH soluble fraction was subjected to Diaion HP-20 column chromatography using H_2O, 20% MeOH, 40% MeOH, 60% H_2O, and MeOH as eluates, successively. Normal-phase HPLC analysis revealed that the fraction eluted with 20% MeOH contained the least amount of tannic acid when compared to the EtOAc and other *n*-BuOH fractions. This fraction was separated by repeated-column chromatography on Toyopearl HW-40 (coarse grade) and MCI-gel CHP-20P and preparative TLC to yield seven phenolic compounds (**1**–**7**).

Compound **1** was obtained as yellowish brown amorphous powder. Its ^{1}H NMR spectrum showed two doublets at δ 6.30 and 7.60 with coupling constants of 16.2 Hz due to *trans* olefinic protons in addition to three doublets at δ 6.82 (1H, d, J= 8.4 Hz), 6.99 (1H, dd, J= 8.4, 2.4 Hz) and 7.09 (1H, d, J= 2.4 Hz) assigned to

one 1,3,4-trisubstituted aromatic ring moiety. Also, the ^{13}C NMR spectrum showed signals at δ 114.1, 115.3, 121.8, 126.6, 145.6, 145.9, 148.4, and 167.5. These observations suggested the presence of a caffeic acid unit[14]. Moreover, signals of three oxymethine protons appeared at δ_H 3.77 (1H, dd, J= 9.0, 3.6 Hz), 4.21 (1H, m), and 5.38 (1H, ddd, J= 13.8, 9.0, 4.2 Hz) in addition to a broad signal for two methylene groups at δ 2.10~2.25 (4H, m) suggesting the presence of one quinic acid moiety[14]. This assignment was supported by the analysis of ^{13}C NMR spectral data that displayed three oxymethines (δ 70.2, 70.8, and 72.4), two methylenes (δ 37.1 and 37.7), one oxygenated quaternary carbon (δ 75.0), and one carboxyl carbon (δ 175.9). The location of caffeoyl substitution on the quinic acid moiety was deduced from the downfield shift of the proton at C-5 (δ 5.38) compared to free quinic acid[15]. By direct comparison with literature data[16] and authentic sample (co-TLC), the structure of compound **1** was identified as 5-*O*-caffeoylquinic acid (chlorogenic acid) (0.0019%).

Compound **2** was isolated as yellowish brown amorphous powder. Its ^{1}H and ^{13}C NMR spectral data are very close to those of **1** except for the appearance of one *p*-coumaric acid unit instead of caffeic acid unit. This was indicated by the appearance of two characteristic doublets for *trans* olefinic protons at δ_H 6.27 and 7.49 (each 2H, J= 16.2 Hz), in addition to two doublets for 1,4-disubstituted aromatic ring at δ_H 6.79 and 7.52 (each 2H, J= 8.4 Hz)[14]. Furthermore, the ^{13}CNMR spectrum displayed characteristic signals at δ 119.9, 121.2, 130.6, 135.7, 149.9, 165.2, and 171.2. Thus, the structure of compound **2** was identified as 5-*O*-coumaroylquinic acid (0.0014%) by comparison of its spectral data with those published in the literature[17].

The UV spectral data in methanol for compounds **3**-**5** suggested their structures as C-3 OH substituted flavonols having free hydroxyl groups at positions 5, 7, 3′ and 4′ [18]. The ^{1}H NMR spectrum of compound **3** revealed a singlet at δ 7.45 (2H, s, H-2′/6′) and one set of *meta*-coupled aromatic protons at δ 6.21 and 6.40 (each 1H, d, J= 1.8 Hz) suggesting a myricetin derivative[18]. Furthermore, the appearance of two anomeric protons at δ 5.10 (1H, d, J= 7.8 Hz) and 4.58 (1H, d, J= 1.8 Hz) in addition to a methyl group at δ 1.27 (3H, d, J= 6.6 Hz) indicated the presence of a β-sugar unit linked to α-rhamnopyranosyl unit[19]. On the basis of the ^{13}C NMR spectral data, the two sugar units were identified as β-galactopyranosyl and α-rhamno-pyranosyl units[19]. The downfield shift of C-6″ (δ 67.4) and the appearance of a cross peak between H-1‴ (δ 4.58) and C-6″ (δ 67.4) indicated the interglycosidic linkage (1‴→6"). Also, the HMBC spectrum showed cross peaks between H-1″ (δ 5.10) and C-3 (δ 136.0) confirming the glycosylation at postion-3. Based on these data and comparison with

literature data[20], compound **3** was determined to be myricetin 3-*O*-α-L-rhamnopyranosyl(1'''→6'')β-D-galactopyranoside (myricetin 3-robinoside) (0.0004%).

The ^{1}H NMR and ^{13}C NMR spectra of compounds **4** and **5** exhibited signals for myricetin derivative resembling those of **3** except for the appearance of β-glucuronic acid unit (δ_C 71.4, 73.8, 76.1, 76.2, 104.0 and 170.0) and β-galactopyranosyl unit (δ_C 60.2, 68.1, 71.4, 73.5, 76.1 and 102.4), respectively, instead of robinoside unit[19]. By comparison of their spectral data with the reported data[21&22], the structures of compounds **4** and **5** were concluded to be myricetin 3-*O*-β-D-glucuronide (0.0009%) and myricetin 3-*O*-β-D-galactopyranoside (0.0004%) respectively.

Compound **6** was obtained as white amorphous powder. Its ^{1}H and ^{13}C NMR spectra displayed signals for two galloyl units [δ_H 7.12 and 7.17 (each 2H, s); δ_C 109.0, 109.4 (C-2/6), 119.9, 120.2 (C-1), 139.2, 139.5 (C-4), 145.3 (C-3/5), 165.8 and 167.1 (CO)] and one glucose moiety [δ_H 3.55~3.75 (4H, m, H-2′,3′,4′,5′), 4.44 (1H, dd, J= 12.0, 5.4 Hz, H-6′b), 4.59 (1H, dd, J= 12.0, 1.8 Hz, H-6′a) and 5.73 (1H, d, J= 7.8 Hz, H-1′); δ_C 63.3 (C-6′), 70.0 (C-4′), 72.9 (C-2′), 75.3 (C-3′), 76.9 (C-5′) and 94.8 (C-1′)][23]. The large coupling constant J= 7.8 Hz indicated the β-configuration of the anomeric center[19]. The placements of the two galloyl units at C-1 and C-6 were deduced from the downfield shifts of H-1′ (δ 5.73) and H-6′a,b (δ 4.44 and 4.59). From the previous evidence and by comparison of its spectral data with the literature data[23], compound **6** was assigned as 1,6-digalloyl-β-D-glucose (0.0002%).

Compound **7** was isolated as white amorphous powder. The ^{1}H NMR spectrum suggested its nature to be a flavan derivative by the appearance of four signals for the aliphatic protons of ring C at δ 2.55 (1H, dd, J= 16.2, 7.8 Hz, H-4b), 2.89 (1H, dd, J= 16.2, 5.4 Hz, H-4a), 4.02 (1H, ddd, J= 7.8, 7.2, 5.4 Hz, H-3), 4.60 (1H, d, J= 7.2 Hz, H-2). The coupling constant of H-2/H-3 (J= 7.8 Hz) indicated its structure as a flavan-3-ol[24]. Furthermore, the spectrum revealed one set of *meta*-coupled aromatic protons at δ 5.90 (1H, d, J= 1.8 Hz, H-6), 5.97 (1H, d, J= 1.8 Hz, H-8) and three aromatic protons of ring B with a characteristic ABX-type coupling at δ 6.75 (1H, dd, J= 8.4, 2.4 Hz, H-6′), 6.80 (1H, d, J= 8.4 Hz, H-5′), 6.88 (1H, d, J= 2.4 Hz, H-2′). The aforementioned spectral data were in accordance with the data published for (+)-catechin[25]. Thus, compound **7** was identified as (+)-catechin (0.0004%).

This is the first report on the occurrence of myricetin glycosides (**3-5**) in the genus *Schinus*. Compounds **1**, **2** and **6** are isolated for the first time from *S. terebinthifolius* Raddi.

The tannic acid content of the EtOAc- and *n*-BuOH-soluble fractions (Fig. 1) from the leaves of

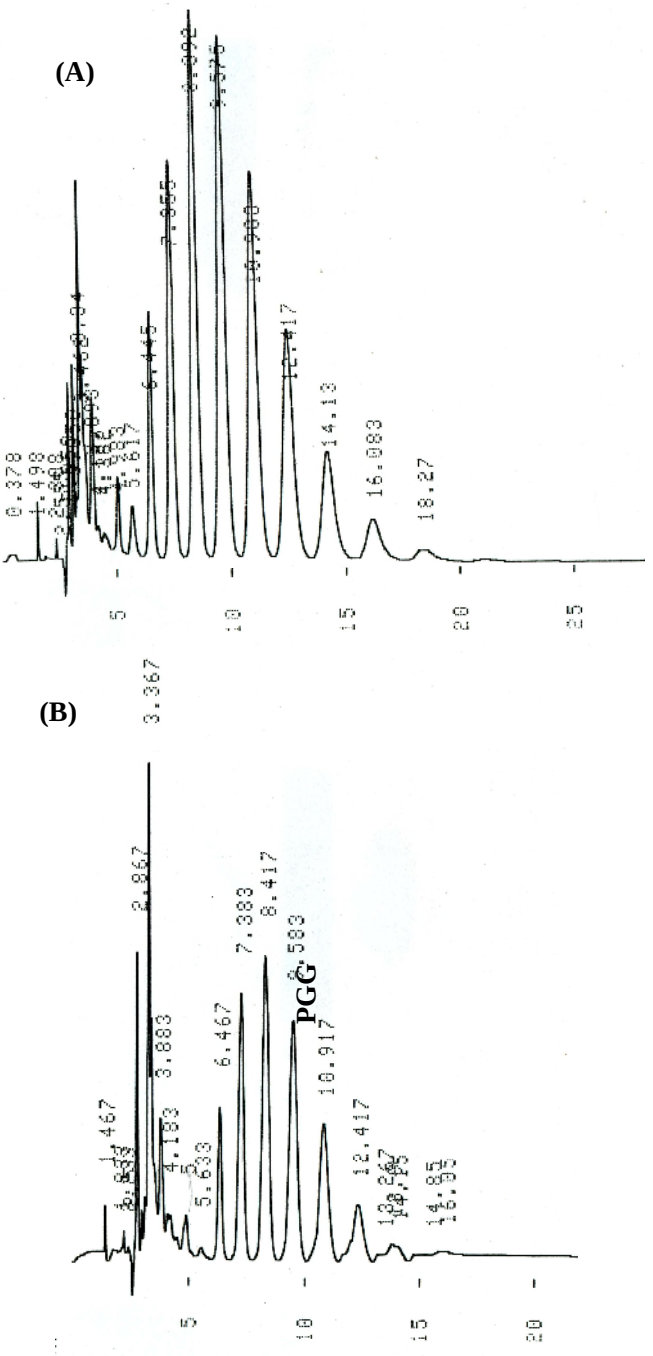

Fig. 1: Normal-phase HPLC investigation of tannic acid content in the leaves of *S. terebinthifolius* Raddi. (**A**) EtOAc-soluble fraction (**B**) *n*-BuOH-soluble fraction.

S. terebinthifolius Raddi were examined by normal-phase HPLC. The results revealed higher amounts of tannic acid in the EtOAc-soluble fraction (79%) than that in the *n*-BuOH-soluble fraction (45%).

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