FLAVONOIDS FROM *GUIZOTIA ABYSSINICA*

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Nine flavonoids, (–)-liquiritigenin (1), (–)-7,3′,4′-trihydroxyflavanone (2), (–)-7,8,3′,4′-tetrahydr oxyflavanone (3), 7,3′,4′-trihydroxylflavone (4), quercetin (5), isoliquiritigenin (6), butein (7), okanin (8), and 3,2′,4′-trihydroxy-4,3′-dimethoxychalcone (9), were isolated from the aerial parts of *Guizotia abyssinica*. The structures of these compounds were identified on the basis of their spectral data and comparison with those in the literature.

Key words: *Guizotia abyssinica*, Asteraceae, aerial part, flavonoid.

INTRODUCTION

Guizotia abyssinica (L.f.) Cass. belongs to the family of Asteraceae and grows in the countries like India and Ethiopiais. *Guizotia abyssinica* is primarily cultivated in India and its seeds have high content of linoleic acid. The oil of the seeds of *G. abyssinica* is traditionally used for treatment of rheumatism.[1,2] The phytochemical study of this plant has not been reported. In our investigation on the chemical constituents of G. *abyssinica*, nine compounds, (–)-liquiritigenin (**1**),[3,4] (–)-7,3′,4′-trihydroxyfla vanone (**2**),[5] (–)-7,8,3′,4′-tetrahydroxylflavanone (**3**),[6] 7,3′,4′-trihydroxyflavone (**4**),[7] quercetin (**5**),[4,8] isoliquiritigenin (**6**),[4,9] butein (**7**),[10] okanin (**8**),[11] and 3,2′,4′-trihydroxy-4,3′-dimethoxychalcone (**9**),[4,10,11] were isolated from the water soluble portion of its MeOH extract. The structures of these compounds were identified on the basis of their spectral analyses and comparison with spectroscopic and physical data in literature.

MATERIALS AND METHODS

General Methods

Optical rotations were recorded on a Jasco DIP-370 polarimeter. IR spectra were measured on a

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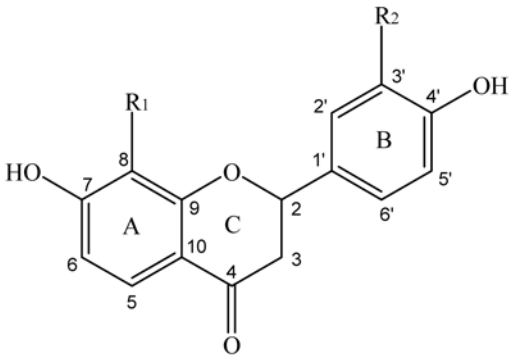
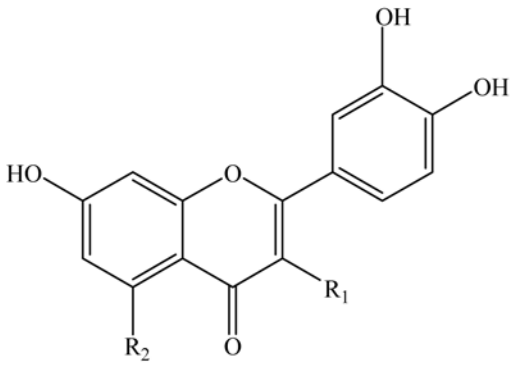
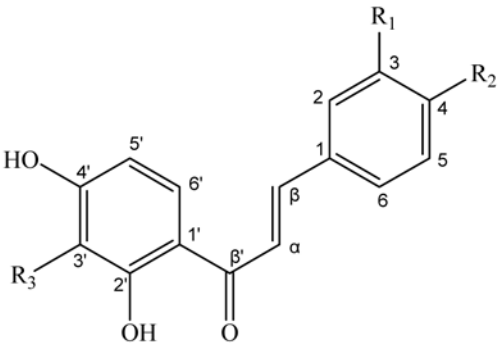


1 R_1=H, R_2=H
2 R_1=H, R_2=OH
3 R_1=OH, R_2=OH



4 R_1=H, R_2=H
5 R_1=OH, R_2=OH



6 R_1=H, R_2=OH, R_3=H
7 R_1=OH, R_2=OH, R_3=H
8 R_1=OH, R_2=OH, R_3=OH
9 R_1=OH, R_2=OMe, R_3=OMe

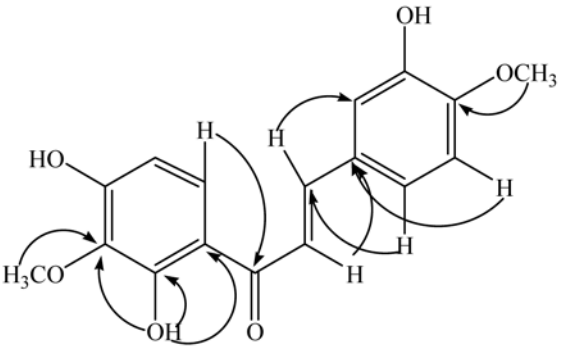


Figure 1. HMBC correlations of **9**.

Nicolet Avatar 320 FT-IR spectrophotometer. EIMS and HREIMS spectra were recorded on a Finnigan MAT GCQ and a Finnigan/Thermo Quest MAT 95XL Mass spectrometers, respectively. The NMR spectra were recorded on a Bruker AC-400 spectrometers. Melting point was determinted on a Yanaco MP-I3 micro melting point apparatus. For thin-layer chromatography analysis, silica gel 60 F_{254} plates (Merck) were used.

Plant Material

The aerial parts of *Guizotia abyssinica* were collected at the Seed Improvement and Propagation Station, Hsinshe, Taichung, Taiwan. The voucher specimen was deposited at the Herbarium of the National Research Institute of Chinese Medicine, R.O.C.

Extraction and Isolation

The air-dried aerial parts of *Guizotia abyssinica* (22 Kg) were extracted at 50°C with MeOH (120 L× 3). After evaporation of the solvent, the concentrated MeOH extract was separated into water-soluble and water-insoluble portions. The water-soluble

portion was subjected to a Diaion HP-20 column and eluted with H_2O and then MeOH to afford H_2O and MeOH fractions. The MeOH fraction (200 g) was rechromatographed on a silica gel column eluting with n-hexane/EtOAc and EtOAc/MeOH mixtures as solvent systems to give 24 fractions (Fr-1~Fr-24). The fraction Fr-5, eluate of n-hexane-EtOAc (5:1), was further chromatographed on a silica gel column eluting with n-hexane-EtOAc (1:1) and Sephadex LH-20 (MeOH) to give (–)-liquiritigenin (**1**, 13.1 mg), isoliquiritigenin (**6**, 29.8 mg), and 3,2′,4′-trihydroxy-4,3′-dimethoxychalcone (**9**, 4.6 mg). The fraction Fr-8, eluate of n-hexane-EtOAc (1:1), was reseparated on a silica gel column eluting with a gradient solvent system of $CHCl_3/Me_2CO$ (5:1 →1:1) to afford five fractions (Fr-8-1~Fr-8-5). The fraction Fr-8-4, eluate of $CHCl_3/Me_2CO$ (2:1), was further purified by silica gel ($CHCl_3/Me_2CO$ = 3:1) and Sephadex LH-20 (MeOH) columns to give (–)-7 ,3',4'-trihydroxyflavanone (**2**, 29.8 mg) and butein (**7**, 10.8 mg). Fraction Fr-8-5, eluate of $CHCl_3/Me_2CO$ (1:1), was purified over silica gel ($CHCl_3/Me_2CO$ = 3:1) and Sephadex LH-20 (MeOH) columns to afford quercetin (**5**, 12.9 mg) and (–)-7,8,3′,4′-tetrahydrox yflavanone (**3**, 23.5 mg). The fraction Fr-10, eluate of n-hexane-EtOAc (1:2), was rechromatographed on a silica gel column eluting with a gradient solvent system of $CHCl_3/Me_2CO$ (5:1→1:1) to afford four fractions (Fr-10-1~Fr-10-4). The fraction Fr-10-2, eluate of $CHCl_3/Me_2CO$ (3:1), was further purified over silica gel ($CHCl_3/Me_2CO$＝3:1) and Sephadex LH-20 (MeOH) columns to obtain 7,3′,4′-trihydroxy flavone (**4**, 2.7 mg). The fraction Fr-10-3, eluate of $CHCl_3/Me_2CO$ (2:1), was purified through a silica gel ($CHCl_3/Me_2CO$ = 2:1) and Sephadex LH-20 (MeOH) columns to afford okanin (**8**, 506.0 mg).

(–)-Liquiritigenin (1)

Brown solid; mp 180-182°C; $[\alpha]_D^{25}$–18.9° (*c* 0.9, MeOH); IR ν_{max} (KBr) cm^{-1}: 3474, 1661, 1603, 1571, 1514, 1472, 1335, 1267, 1162; ^1H NMR (400 MHz, acetone-d_6) δ: 2.62 (1H, dd, *J*=2.8, 16.8 Hz, H-3), 3.00 (1H, dd, *J*=12.8, 16.8 Hz, H-3), 5.40 (1H, dd, *J*=2.8, 12.8 Hz, H-2), 6.38 (1H, d, *J*=2.4 Hz, H-8), 6.54 (1H, dd, *J*=2.4, 8.8 Hz, H-6), 6.87 (2H, d, *J*=8.8 Hz, H-3′, 5′), 7.36 (2H, d, *J*=8.8 Hz, H-2′, H-6′), 7.68 (1H, d, *J*=8.8 Hz, H-5); ^{13}C NMR (100 MHz, acetone-d_6) δ: 43.8 (C-3), 79.5 (C-2), 102.8 (C-8), 110.9 (C-6), 113.5 (C-10), 115.2 (C-3′ and C-5′), 128.0 (C-2′ and C-6′), 128.5 (C-5), 130.4 (C-1′), 157.7 (C-4′), 163.8 (C-9), 165.9 (C-7), 189.6 (C-4); EIMS *m/z* (rel. int.): 256 $[M]^+$ ($C_{15}H_{12}O_4$, 100), 239 (12), 163 (11), 150 (12), 137 (37), 120 (15).

(–)-7,3',4'-Trihydroxyflavanone (2)

Yellow syrup; $[\alpha]_D^{25}$–38.8° (*c* 0.8, MeOH); IR ν_{max} (KBr) cm^{-1}: 3274, 1650, 1608, 1461, 1324, 1277, 1156, 1114, 809; ^1H NMR (400 MHz, acetone-d_6) δ: 2.68 (1H, dd, *J*=2.8, 16.8 Hz, H-3), 3.00 (1H, dd, *J*=12.8, 16.8 Hz, H-3), 5.31 (1H, dd, *J*=2.8, 12.8 Hz, H-2), 6.35 (1H, d, *J*=2.4 Hz, H-8), 6.49 (1H, dd, *J*=2.4, 8.8 Hz, H-6), 6.73 (1H, d, *J*=8.0 Hz, H-5′), 6.72 (1H, dd, *J*=2.0, 8.0 Hz, H-6′), 6.92 (1H, d, *J*=2.0 Hz, H-2′), 7.72 (1H, d, *J*=8.8 Hz, H-5); ^{13}C NMR (100 MHz, acetone-d_6) δ: 44.1 (C-3), 79.9 (C-2), 103.1 (C-8), 110.5 (C-6), 114.0 (C-2′), 114.6 (C-10), 115.3 (C-5′), 118.5 (C-6′), 128.8 (C-5), 131.4 (C-1′), 145.3 (C-4′), 145.6 (C-3′), 163.8 (C-9), 164.6 (C-7), 189.9 (C-4); EIMS *m/z* (rel. int.): 272 $[M]^+$ ($C_{15}H_{12}O_5$, 100), 255 (18), 163 (17), 150 (48), 137 (40).

(–)-7,8,3',4'-Tetrahydroxyflavanone (3)

Yellow syrup, $[\alpha]_D^{25}$–110.0° (*c* 0.3, MeOH); IR

ν_{max} (KBr) cm^{-1}: 3358, 1656, 1608, 1524, 1456, 1319, 1282; ^{1}H NMR (400 MHz, acetone-d_6) δ: 2.64 (1H, dd, J=2.8, 16.8 Hz, H-3), 3.01 (1H, dd, J=12.8, 16.8 Hz, H-3), 5.37 (1H, dd, J=2.8, 12.8 Hz, H-2), 6.58 (1H, d, J=8.8 Hz, H-6), 6.86 (1H, d, J=8.0 Hz, H-5′), 6.85 (1H, dd, J=1.6, 8.0 Hz, H-6′), 7.03 (1H, d, J=1.6 Hz, H-2′), 7.28 (1H, d, J=8.8 Hz, H-5); ^{13}C NMR (100 MHz, acetone-d_6) δ: 44.1 (C-3), 80.3 (C-2), 109.6 (C-6), 114.0 (C-2′), 114.8 (C-10), 115.0 (C-5'), 117.9 (C-5), 118.4 (C-6′), 131.0 (C-1′), 132.7 (C-8), 145.1 (C-3′), 145.5 (C-4′), 150.8 (C-9), 151.7 (C-7), 190.2 (C-4); EIMS *m/z* (rel. int.): 288 $[M]^+$ ($C_{15}H_{12}O_6$, 100), 153 (70), 136 (12).

7,3',4'-Trihydroxyflavone (4)

Yellow solid; mp 223-225°C; IR ν_{max} (KBr) cm^{-1}: 3411, 1671, 1603, 1508, 1451, 1277, 1125, 1109; ^{1}H NMR (400 MHz, acetone-d_6) δ: 6.61 (1H, s, H-3), 6.76 (1H, dd, J=1.6, 8.4 Hz, H-6), 6.80 (1H, d, J=1.6 Hz, H-8), 6.92 (1H, d, J=8.0 Hz, H-5′), 7.32 (1H, dd, J=2.0, 8.0 Hz, H-6′), 7.55 (1H, d, J=2.0 Hz, H-2′), 7.59 (1H, d, J=8.4 Hz, H-5); ^{13}C NMR (100 MHz, acetone-d_6) δ: 98.5 (C-8), 111.5 (C-3), 112.6 (C-6), 114.0 (C-10), 115.6 (C-5′), 117.8 (C-2′), 124.5 (C-1′), 124.7 (C-6′), 125.5 (C-5), 145.4 (C-3′), 146.3 (C-2), 147.5 (C-4′), 165.9 (C-7), 168.0 (C-9), 181.6 (C-4); EIMS *m/z* (rel. int.): 270 $[M]^+$ ($C_{15}H_{10}O_5$, 100), 253 (18), 242 (10), 213 (11), 195 (13), 163 (12), 137 (19).

Quercetin (5)

Yellow solid; mp 273-275°C; IR ν_{max} (KBr) cm^{-1}: 3421, 1661, 1614, 1519, 1445, 1356, 1319, 1256, 1167; ^{1}H NMR (400 MHz, acetone-d_6) δ: 6.25 (1H, d, J=2.0 Hz, H-6), 6.57 (1H, d, J=2.0 Hz, H-8), 6.98 (1H, d, J=8.8 Hz, H-5′), 7.68 (1H, dd, J=2.0, 8.8 Hz, H-6′), 7.81 (1H, d, J=2.0 Hz, H-2′), 12.1 (1H, s, 5-OH); ^{13}C NMR (100 MHz, acetone-d_6) δ: 94.5 (C-8), 99.2 (C-6), 104.1 (C-10), 115.8 (C-2′), 116.2 (C-5′), 121.5 (C-6′), 123.8 (C-1′), 136.8 (C-3), 145.9 (C-3′), 147.0 (C-2), 148.1 (C-4′), 157.8 (C-9), 162.3 (C-5), 165.1 (C-7), 176.6 (C-4); EIMS *m/z* (rel. int.): 302 $[M]^+$ ($C_{15}H_{10}O_7$, 100), 284 (55), 274 (12), 229 (9).

Isoliquiritigenin (6)

Orange solid; mp 189-191°C; IR ν_{max} (KBr) cm^{-1}: 3343, 1629, 1598, 1503, 1451, 1367, 1235, 1120; ^{1}H NMR (400 MHz, acetone-d_6) δ: 6.44 (1H, d, J=1.2 Hz, H-3′), 6.45 (1H, dd, J=1.2, 8.8 Hz, H-5′), 6.92 (2H, d, J=8.4 Hz, H-3, H-5), 7.73 (2H, d, J=8.4 Hz, H-2, H-6), 7.76 (1H, d, J=15.2 Hz, H-α), 7.83 (1H, d, J=15.2 Hz, H-β), 8.11 (1H, d, J=8.8 Hz, H-6′), 13.6 (1H, s, 2′-OH); ^{13}C NMR (100 MHz, acetone-d_6) δ: 103.7 (C-3′), 108.7 (C-5′), 114.4 (C-1′), 116.7 (C-3 and C-5), 118.2 (C-α), 127.5 (C-1), 131.7 (C-6), 131.8 (C-2), 133.2 (C-6′), 145.1 (C-β), 161.0 (C-4), 165.7 (C-4′), 167.6 (C-2′), 192.8 (C-β'); EIMS *m/z* (rel. int.): 256 $[M]^+$ ($C_{15}H_{12}O_4$, 100), 293 (13), 163 (12), 150 (16), 137 (32).

Butein (7)

Orange solid; mp 205-207°C; IR ν_{max} (KBr) cm^{-1}: 3295, 1640, 1587, 1550, 1508, 1351, 1288, 1235, 1146; ^{1}H-NMR (400 MHz, acetone-d_6) δ: 6.35 (1H, d, J=2.4 Hz, H-3′), 6.46 (1H, dd, J=2.4, 8.8 Hz, H-5′), 6.90 (1H, d, J=8.0 Hz, H-5), 7.21 (1H, dd, J=2.0, 8.0 Hz, H-6), 7.34 (1H, d, J=2.0 Hz, H-2), 7.68 (1H, d, J=15.2 Hz, H-α), 7.76 (1H, d, J=15.2 Hz, H-β), 8.10 (1H, d, J=8.8 Hz, H-6′), 13.6 (1H, s, 2′-OH); ^{13}C NMR (100 MHz, acetone-d_6) δ: 102.9 (C-3′), 107.8 (C-5'), 113.6 (C-1′), 115.1 (C-2), 117.4

(C-*α*), 122.6 (C-6), 127.3 (C-1), 132.4 (C-6′), 144.7 (C-*β*), 145.5 (C-3), 148.4 (C-4), 155.5 (C-5), 164.7 (C-4′), 166.7 (C-2′), 191.9 (C-*β*'); EIMS *m/z* (rel. int.): 272 $[M]^+$ ($C_{15}H_{12}O_5$, 100), 255 (12), 163 (13), 150 (41), 137 (35).

Okanin (8)

Organe solid; mp 219-221°C; IR ν_{max} (KBr) cm^{-1}: 3385, 1635, 1566, 1503, 1440, 1109, 1020, 972, 836; ^1H NMR (400 MHz, acetone-d_6) δ: 6.49 (1H, d, J=8.8 Hz, H-5'), 6.90 (1H, d, J=8.0 Hz, H-5), 7.22 (1H, dd, J=2.0, 8.0 Hz, H-6), 7.35 (1H, d, J=2.0 Hz, H-2), 7.68 (1H, d, J=15.2 Hz, H-*α*), 7.69 (1H, d, J=8.8 Hz, H-6′), 7.76 (1H, d, J=15.2 Hz, H-*β*); ^{13}C NMR (100 MHz, acetone-d_6) δ: 108.2 (C-5'), 114.7 (C-1′), 115.9 (C-2), 116.3 (C-5), 118.3 (C-*α*), 123.1 (C-6′), 123.4 (C-6), 128.1 (C-1), 133.2 (C-3′), 145.5 (C-*β*), 146.3 (C-3), 149.2 (C-4), 152.5 (C-4′), 154.2 (C-2′), 193.3 (C-*β*′); EIMS *m/z* (rel. int.) 288 $[M]^+$ ($C_{15}H_{12}O_6$, 100), 153 (66), 136 (11).

3,2′,4′-Trihydroxy-4,3′-dimethoxychalcone (9)

Orange solid; mp 154-156°C; IR ν_{max} (KBr) cm^{-1}: 3379, 1629, 1592, 1556, 1508, 1440, 1351, 1267, and 1214; ^1H NMR (400 MHz, acetone-d_6) δ: 3.84 (3H, s, 3′-OCH_3), 3.93 (3H, s, 4-OCH_3), 6.48 (1H, d, J=8.8 Hz, H-5′), 6.90 (1H, d, J=8.0 Hz, H-5), 7.34 (1H, dd, J=1.6, 8.0 Hz, H-6), 7.53 (1H, d, J=1.6 Hz, H-2), 7.79 (1H, d, J=15.6 Hz, H-*α*), 7.84 (1H, d, J=15.6 Hz, H-*β*), 7.34 (1H, d, J=8.8 Hz, H-6′), 13.8 (1H, s, 2′-OH); ^{13}C NMR (100 MHz, acetone-d_6) δ: 56.4 (3′-OCH_3), 60.5 (4-OCH_3), 108.2 (C-5′), 112.0 (C-2), 115.2 (C-1′), 116.2 (C-5), 118.4 (C-*α*), 125.1 (C-6), 127.4 (C-6′), 127.9 (C-1), 135.8 (C-3′), 145.8 (C-*β*), 148.8 (C-3), 150.7 (C-4), 157.5 (C-4′), 159.7 (C-2′), 193.4 (C-*β*′); EIMS *m/z* (rel. int.): 316 $[M]^+$ (100), 301 (13), 284 (14), 180 (16), 167 (43); HREIMS *m/z* $[M]^+$ 316.0948, (calad. for $C_{17}H_{16}O_6$, 316.0947).

RESULTS AND DISCUSSION

The MeOH extract of the aerial parts of *Guizotia abyssinica* was separated into water-soluble and water-insoluble portions. The water-soluble portion was successively chromatographed using Diaion HP-20, silica gel and Sephadex LH-20 columns to obtain nine flavonoids.

Compound **1** was obtained as an orange solid. The molecular formula was established to be $C_{15}H_{12}O_4$ based on its EIMS and NMR spectral data. In ^1H NMR spectrum of **1**, the presence of a pair of methylene signals at δ 2.62 (1H, dd, J=2.8, 16.8 Hz, H-3) and 3.00 (1H, dd, J=12.8, 16.8 Hz, H-3) and an O-linked methine signal at δ 5.40 (1H, dd, J=2.8, 12.8 Hz, H-2) suggested that compound **1** was an analogue of flavanone. The rest of signals were assigned to one set of protons of ABX-type ring A [δ 6.38 (1H, d, J=2.4 Hz, H-8), 6.54 (1H, dd, J=2.4, 8.8 Hz, H-6), 7.68 (1H, d, J=8.8 Hz, H-5)] and the other set of protons of AA′BB′-type ring B [δ 6.87 (2H, d, J=8.8 Hz, H-3′,5′), 7.36 (2H, d, J=8.8 Hz, H-2′,6′)]. Based on the analyses of 2D (^1H-^1H COSY, HMQC, and HMBC) spectral data of **1** and comparison of their spectral data with those in literature,[3,4] compound **1** was identified as (–)-liquiritigenin.

Compounds **2** and **3** were obtained as yellow syrup. The spectral characteristics of two compounds showed that they were also analogues of flavanone. The ^1H and ^{13}C NMR spectra of **2** were similar to those of **1**, except for the ring B moiety which

beared one set of ABX-type protons [δ 6.72 (1H, dd, J=2.0, 8.0 Hz, H-6′), 6.73 (1H, d, J=8.0 Hz, H-5′), and 6.92 (1H, d, J=2.0 Hz, H-2′)]. This was supported by the presence of a molecular ion peak at *m/z* 272 ($C_{15}H_{12}O_5$) in EIMS of **2**, which was 16 mass units larger than that of **1**. Based on the above evidence and comparison with those in the literature,[5] compound **2** was assigned as (–)-7,3′,4′-trihydrox yflavanone. The spectral data of **3** were similar to those of **2**, except for the ring A moiety. A pair of o-coupling doublets (J=8.8 Hz) attributed to H-5 and H-6 were shown in the ^{1}H NMR spectrum of **3**, and C-8 signal was shifted downfield to appear at δ 132.7. Therefore, compound **3** was determined to be (–)-7,8, 3′,4′-tetrahydroxyflavanone, which was confirmed by comparison with literatural data.[6]

Compound **4** and **5** were obtained as yellow solid. The molecular formula of **4** was derived as $C_{15}H_{10}O_5$ from its EIMS, ^{1}H NMR and ^{13}C NMR data. The spectral characteristics of **4** were resemble to those of **2**, except for the presence of one typical singlet at δ 6.61 attributed to H-3 in the ^{1}H NMR spectrum of **4**, which indicated that compound **4** was a flavone analogue. The remaining proton signals included two sets of ABX-type signals. One set appeared at δ 6.76 (1H, dd, J=1.6, 8.4 Hz, H-6), 6.80 (1H, d, J=1.6 Hz, H-8), and 7.59 (1H, d, J=8.4 Hz, H-5) and the other set appeared at 6.92 (1H, d, J=8.0 Hz, H-5′), 7.32 (1H, dd, J=2.0, 8.0 Hz, H-6'), and 7.55 (1H, d, J=2.0 Hz, H-2'). Based on the above data and comparison with those in literature,[7] the structure of **4** was identified as 7,3′,4 ′-trihydroxyflavone. Compound **5** had a molecular formula of $C_{15}H_{10}O_7$. Comparing the spectral data of **5** with those of **4**, the proton signal H-3 was absent and C-3 signal was shifted downfield to appear at δ 136.8, suggesting that compound **5** was a flavonol analogue. In addition, a pair of *m*-coupling doublets at δ 6.25 (J=2.0 Hz) and 6.57 (J=2.0 Hz) attributed to H-6 and H-8 were observed. Thus, the structure of compound **5** was identified as quercetin.[4,8]

Compounds **6~9**, were obtained as orange solid and they belonged to the chalcone derivatives. Compound **6** had a $C_{15}H_{12}O_4$ derived from its EIMS data. The IR bands at 3343 and 1629 cm^{-1} indicated the presence of hydroxyl and carbonyl groups. The ^{13}C NMR spectrum of **6** showed fifteen carbon signals including one carbonyl group (δ 192.8). In its ^{1}H NMR spectrum, the presence of two doublets with a *trans* configuration at δ 7.76 (1H, d, J=15.2 Hz, H-α) and 7.83 (1H, d, J=15.2 Hz, H-β) suggested that compound **6** belonged to a chalcone analogue. Other proton signals included a chelated hydroxyl singlet at δ 13.6, one set of ABX-type signals at δ 6.44 (1H, d, J=1.2 Hz, H-3′), 6.45 (1H, dd, J=1.2, 8.8 Hz, H-5′), and 8.11 (1H, d, J=8.8 Hz, H-6′), and another set of AA′BB′-type signals at δ 6.92 (2H, d, J=8.4 Hz, H-3, H-5) and 7.73 (2H, d, J=8.4 Hz, H-2, H-6). From the above data, the structure of 6 was thus determined to be isoliquiritigenin.[4,9]

Compounds **7** and **8** had molecular formulas of $C_{15}H_{12}O_5$ and $C_{15}H_{12}O_6$, respectively. Comparing their ^{1}H NMR spectra with that of **6**, the ABX-type signals were replaced by the AA′BB′-type signals on ring B. Besides, a pair of *o*-coupling doublets at δ 6.49 (1H, d, J=8.8 Hz, H-5′) and 7.69 (1H, d, J=8.8 Hz, H-6′) were shown in the ^{1}H NMR spectrum of **8**. Therefore, the structures of compounds **7** and **8** were identified as butein[10] and okanin,[11] respectively.

Compound **9** had a molecular formula of $C_{17}H_{16}O_6$ derived from HREIMS data. Its ^{1}H and ^{13}C NMR spectral characteristics were closely

similar to those of **8**. The DEPT (δ 56.4 and 60.5) and ^{1}H NMR (δ 3.84 and 3.93) spectra of **9** showed the presence of two methoxyl groups which existed HMBC correlations with the carbon signals at δ 135.8 (C-3′) and δ 150.7 (C-4). Thus, the structure of **9** was identified as 3,2′,4′-trihydroxy-4,3′-dimethylchalcone.[4,10,11]

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REFERENCES

1. Vles RO, Gottenbos JJ. Nutritional characteristics and food uses of vegetable oils. "Oil crops of the world", Mcgraw Hill, New York, America, pp.394-403, 1989.
2. Dutta PC, Helmersson S, Eshetu K, Getinet A, Appelqvist LA. Variation in lipid composition of niger seed (*Guizotia abyssinica* Cass.) samples collected from different regions in Ethiopia. J. Am. Chem. Soc. 71:839-843, 1994.
3. Miyase T, Fukushima S, Akiyama Y. Studies on the constituents of *Hedysarum polybortrys* HAND.-MAZZ.. Chem. Pharm. Bull. 32:3267-3270, 1984.
4. Youssef DTA, Ramadan MA, Khalifa AA. Acetophenones, a chalcone, a chromone and flavonoids from *Pancratium maritimum*. Phytochemistry 49:2579-2583, 1998.
5. Kitanaka S, Takido M. Demethyltorosaflavones C and D from *Cassia nomame*. Phytochemistry 31:2927-2929, 1992.
6. Foo LY. Configuration and conformation of dihydroflavonols from *Acacia melanoxylon*. Phytochemistry 26:813-817, 1987.
7. van Acker FAA, Hageman J A, Haenen GRMM, van der Vijgh WJF, Bast A, Menge WMPB. Synthesis of novel 3,7-substituted-2-(3′,4′-dihydroxyphenyl)flavones with improved antioxidant activity. J. Med. Chem. 43:3752-3760, 2000.
8. Wawer I, Zielinska A. Solid state nuclear Magnetic Resonance 10, pp.33-38, 1997.
9. Veitch NC, Sutton PSE, Kite G.C, Ireland HE. Six new isoflavones and a 5-deoxyflavonol glycoside from the leaves of *Ateleia Herbert-smithii*. J. Nat. Prod. 66:210-216, 2003.
10. Namikoshi M, Nakata H, Nuno M, Ozawa T, Saitoh T. Homoisoflavonoids and related compounds. Ⅲ. phenolic constituents of *Caesalpinia japonica* SIEB. et ZUCC.. Chem. Pharm. Bull. 35:3568-3575, 1987.
11. Hoffmann B, Hölzl J. Chalcone glucosides from *Bidens pilosa*. Phytochemistry 28:247-249, 1989.

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印度油菊之類黃酮化學成分研究

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印度油菊（*Guizotia abyssinica* (L.f.) Cass.）之地上莖部甲醇抽出物，經各種色層分析法分離得到九個類黃酮化合物包括(–)-liquiritigenin (1)、(–)-7,3′,4′-trihydroxyflavanone (2)、(–)-7,8,3′,4′-tetrahydroxyflavanone (3)、7,3′,4′-trihydroxyflavone (4)、quercetin (5)、isoliquiritigenin (6)、butein (7)、okanin (8)及3,2′,4′-trihydroxy-4,3'-dimethoxychalcone (9)。這些化合物皆經由質譜及核磁共振光譜的解析而確認其結構。

關鍵詞：印度油菊，翠菊科，地上莖部，類黃酮。

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