Two New Prenylated Flavonoids from Paracalyx scariosa

Mokhtar Ali Nia, K. V. Rao, K. Sreeramulu, and D. Gunasekar

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TWO NEW PRENYLATED FLAVONOIDS FROM *PARACALYX SCARIOSA*

MOKHTAR ALI NIA, K.V. RAO, K. SREERAMULU, and D. GUNASEKAR*

Department of Chemistry, Sri Venkateswara University, Tirupati 517 502, India

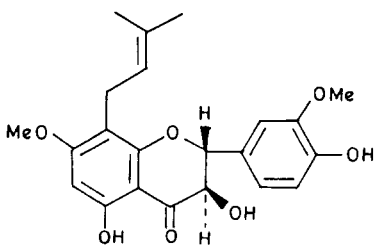
ABSTRACT.—Two new prenylated flavonoids, scariosin [**1**] and isorhynchospermin [**2**], were isolated from the leaves of *Paracalyx scariosa* (Fabaceae), together with kaempferol, quercetin, kaempferol-3-*O*-rutinoside, and rutin. The structures were characterized as (2*R*,3*R*)-7,3′-dimethoxy-8-*C*-prenyltaxifolin [**1**] and 7,4′-dimethoxy-6-*C*-prenylquercetin [**2**] by their chemical and spectral data.

Paracalyx scariosa Roxb. (Fabaceae) (1) is the only species of this genus that grows in India, and it has not been phytochemically investigated, so far. We have examined the leaves and in this paper report the isolation and characterization of a new prenylated dihydroflavonol, scariosin [**1**], and a new prenylated flavonol, isorhynchospermin [**2**], along with kaempferol, quercetin, kaempferol-3-*O*-rutinoside, and rutin.

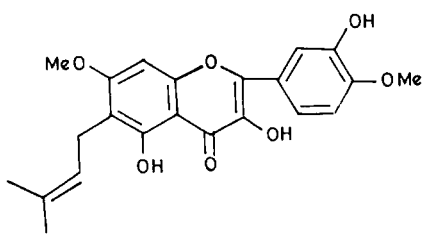
RESULTS AND DISCUSSION

The petroleum ether extract of *P. scariosa* was column chromatographed over Si gel to yield scariosin [**1**]. The color reactions and uv spectrum of **1** resembled those of a dihydroflavonol (2) with λ max (MeOH) at 290 and an inflection at 342 nm. The ir spectrum exhibited absorptions at 3425 (chelated hydroxyl), 1630 (conjugated carbonyl), and 1360 cm^{-1} (gem dimethyl). The ^{1}H-nmr spectrum exhibited the typical AB system due to H-2 and H-3 of dihydroflavonol (2) at δ 5.05 (d, $J = 11$ Hz) and δ 4.48 (d, $J = 11$ Hz), respectively. The 3-OH was found as a doublet ($J = 6$ Hz) at δ 5.78 by coupling with H-3. The presence of a *C*-linked prenyl residue (3,4) in scariosin [**1**] was evidenced from the signals at δ 5.10 (vinyl proton), 3.10 (allylic protons), and 1.55 (vinyl methyls). Two three-proton singlets at δ 3.90 and 3.82 showed the presence of two MeO groups, and the former was assigned to the 7 position based on the fact that there was no bathochromic shift of the uv absorption maximum with NaOAc. A broad signal at δ 12.08 was assigned to the chelated 5-OH.

The presence of three OH groups in **1** was evidenced by the formation of a triacetate ([M]$^+$ 526). The appearance of one H-2′ doublet (δ 7.23) downfield (0.18 ppm) from the H-6′ double doublet (δ 7.05) supported ring B with a 3′-MeO and 4′-OH substitution pattern. The downfield shift (0.24 ppm) of the signal (δ 6.06) for the aromatic singlet of ring A upon acetylation (5), and a bathochromic shift of 25 nm in the uv spectrum after the addition of $AlCl_3$ (6) indicated that it must be ortho to 5-OH. Thus, the prenyl residue in scariosin [**1**] was shown to be located at the C-8 position. A trans orientation of the C-ring



1



2

methine protons was inferred from the large *J* value (11 Hz) which is typical of diaxial coupling (3). Positive optical rotation of **1** indicated the 2*R*,3*R* configuration (7); thus, the structure of scariosin was established as (2*R*,3*R*)-7,3′-dimethoxy-8-*C*-prenyltaxifolin [**1**]. Confirmation of this structure was obtained from the low resolution eims of **1** which exhibited the molecular ion at *m/z* 400. Two mass fragments at *m/z* 235 and 166 consistent with RDA fragmentation followed by hydrogen transfer showed one OH, one MeO, and an isoprenyl group in ring A, and a MeO and OH in ring B.

Isorhynchospermin [**2**], isomeric with rhynchospermin (8), was obtained as yellow needles from the MeOH-soluble part of the C_6H_6 extract by preparative tlc. The uv absorption data of the compound were similar to those of a flavonol (2). A bathochromic shift of 60 nm with $AlCl_3$ clearly showed the presence of a free 3-OH group. Absence of bathochromic shifts with NaOAc and NaOMe showed substitution at the 7 and 4′ positions. Its ^{1}H-nmr spectrum exhibited two singlets at δ 3.90 and 3.85 indicating two MeO groups. The presence of a *C*-linked prenyl residue was inferred from the signals at δ 1.68, 1.76, 3.42, and 5.15. The A-ring aromatic proton appearing as a singlet at δ 6.58 was asigned to H-8 on the basis of comparison with the chemical shift value of δ 6.41 exhibited by H-6 of rhynchospermin (8). The signal due to H-2′ in the acetylated compound appeared at δ 7.52, slightly higher field than the H-6′ signal at δ 7.70. This behavior is characteristic for a flavonol containing 4′-MeO–3′-OH substitution (9). Thus, isorhynchospermin [**2**] appears to be a *C*-prenylated ombuin containing two MeO groups at the 4′ and 7 positions and the prenyl residue at the 6 position. The eims of **2** gave the molecular ion peak at *m/z* 398 and fragments at *m/z* 179 and 151, which confirmed the presence of a prenyl group in ring A and confirmed the structure as 7,4′-dimethoxy-6-*C*-prenylquercetin [**2**]. This proposal was in agreement with the ^{13}C-nmr spectral data. Isorhynchospermin [**2**] was shown to be identical in all respects with the sample of the dehydro-derivative of isotirumalin obtained from *Rhynchosia cyanosperma* (10).

The Me_2CO extract on solvent fractionation followed by preparative pc gave kaempferol, quercetin, kaempferol-3-*O*-rutinoside, and rutin, which were identified by spectral and chemical studies.

EXPERIMENTAL

INSTRUMENTATION.—Mass spectra were obtained on a VG Instruments VG-70 instrument in the ei mode at 70 eV. Ir spectra were run on a Beckman Model 4244 instrument using KBr pellets, and uv spectra on a Beckman 25 spectrophotometer. All nmr experiments were performed on a Nicolet NT 300 WB or JEOL-FX-90Q spectrometer equipped with 5 mm ^{1}H and ^{13}C probes operating at 300.06 and 75.45, or 90 and 22.5 MHz, respectively. Samples were run in $CDCl_3$ or DMSO-d_6, and chemical shifts were referred to internal TMS (0.00 ppm).

PLANT MATERIAL.—Leaves of *P. scariosa* were collected at Araku Valley in Andhra Pradesh, India, in November 1988. A voucher specimen has been deposited in the Herbarium of Sri Venkateswara University.

EXTRACTION AND ISOLATION.—Shade-dried leaves (1.5 kg) were extracted with petroleum ether, C_6H_6, and Me_2CO. Concentration of the petroleum ether extract under reduced pressure gave a greenish yellow residue (3.5 g) which was dissolved in MeOH (100 ml) and kept in the freezer overnight. The sparingly soluble waxes that separated were filtered, and the procedure was repeated until no more waxes separated on further cooling. The MeOH filtrate was concentrated to a pale yellow solid (350 mg) and was column chromatographed on Si gel (50 g) packed in petroleum ether, petroleum ether/C_6H_6, C_6H_6, C_6H_6/$CHCl_3$, $CHCl_3$, and $CHCl_3$/EtOAc. A total of 50 fractions of 25 ml each were collected and combined on the basis of tlc. Fractions 26–50 were combined to give 50 mg of a pale yellow solid which on crystallization from MeOH gave 35 mg of colorless needles of scariosin [**1**].

The pale yellow solid (140 mg) obtained from the C_6H_6 extract was macerated with 150 ml of MeOH and filtered. The MeOH-soluble part was purified by preparative tlc using C_6H_6-dioxane-HOAc (90:25:4) to give a band at R_f 0.92, which was eluted and crystallized with MeOH to yield pale yellow needles (130 mg) of isorhynchosper-

min [**2**]. The Et_2O- and EtOAc-soluble fractions of Me_2CO extract, on further purification by preparative pc [*n*-BuOH–HOAc–H_2O (4:1:5)], gave kaempferol (80 mg) and quercetin (100 mg), and kaempferol-3-*O*-rutinoside (45 mg) and rutin (40 mg), respectively. These known compounds were identified by spectral and chemical means.

Scariosin [**1**].—Mp 190°. Found C 65.90, H 6.38; $C_{22}H_{24}O_7$ requires C 65.99, H 6.04%. $[\alpha]^{25}D$ +55.4° (*c* = 1.2, pyridine); uv λ max (MeOH) nm (log ε) 290 (4.15), 342 sh (3.50), +$AlCl_3$ 270, 315, +NaOAc 289, 342, +NaOAc/H_3BO_3 292, 318 sh; ir (KBr) cm^{-1} 3425, 1630, 1360, 1235; eims (rel. int.) *m/z* $[M]^+$ 400 (38), 383 (5), 371 (20), 345 (2), 247 (6), 235 (47), 219 (15), 191 (20), 179 (100), 166 (19), 137 (25); ^1H nmr (300 MHz, DMSO-d_6) δ 12.08 (1H, br s, 5-OH; exchangeable in D_2O), 9.12 (1H, br s, 4′-OH; exchangeable in D_2O), 7.23 (1H, d, 2.5 Hz, H-2′), 7.05 (1H, dd, 8.5 and 2.5 Hz, H-6′), 6.88 (1H, d, 8.5 Hz, H-5′), 6.06 (1H, s, H-6), 5.78 (1H, d, 6.0 Hz, 3-OH; exchangeable in D_2O), 5.10 (1H, m, H-2″), 5.05 (1H, d, 11 Hz, H-2), 4.48 (1H, d, 11 Hz, H-3), 3.90 (3H, s, 7-OMe), 3.82 (3H, s, 3′-OMe), 3.10 (2H, d, 8.0 Hz, H-1″), 1.55 (6H, m, H-4″ and -5″).

Triacetate of **1**.—Mp 89°; eims (rel. int.) *m/z* $[M]^+$ 526 (3), 484 (100), 442 (12), 424 (36), 409 (25), 382 (15), 314 (8), 290 (15), 286 (10), 248 (15), 233 (35), 219 (50), 206 (70), 195 (25), 191 (20), 179 (70), 166 (70), 164 (29), 137 (20); ^1H nmr (300 MHz, $CDCl_3$) δ 7.20–7.45 (2H, m, H-6′ and -2′), 6.98 (1H, d, 8.5 Hz, H-5′), 6.30 (1H, s, H-6), 5.62 (1H, d, 12 Hz, H-2), 5.25 (1H, d, 12 Hz, H-3), 5.08 (1H, m, H-2″), 3.93 (6H, s, 3′-OMe and 7-OMe), 3.25 (2H, d, 8 Hz, H-1″), 2.35 (3H, s, 5-OAc), 2.33 (3H, s, 4′-OAc), 2.05 (3H, s, 3-OAc), 1.62 and 1.55 (6H, 2s, H-4″ and -5″).

Isorhynchospermin [**2**].—Mp 190°. Found C 66.04, H 5.25; $C_{22}H_{22}O_7$ requires C 66.32, H 5.57%. Uv λ max (MeOH) nm (log ε) 262 (4.22), 272 sh (4.18), 310 sh (3.91), 382 (4.20), +$AlCl_3$ 271, 310 sh, 363, 442, +$AlCl_3$/HCl 271, 310 sh, 363, 442, +NaOMe 272, 350 sh, 435, +NaOAc 262, 410, +NaOAc/H_3BO_3 262, 310 sh, 382; ir (KBr) cm^{-1} 3520, 3240, 1650, 1620, 1598, 1550, 1420, 1355, 1260; eims (rel. int.) *m/z* $[M]^+$ 398 (100), 383 (84), 369 (6), 368 (3), 367 (3), 343 (11), 330 (45), 315 (6), 179 (6), 151 (14); ^1H nmr (300 MHz, DMSO-d_6) δ 12.50 (1H, s, 5-OH), 7.76 (1H, dd, 8.0 and 2.5 Hz, H-6′), 7.70 (1H, d, 2.5 Hz, H-2′), 7.10 (1H, d, 8 Hz, H-5′), 6.58 (1H, s, H-8), 5.15 (1H, m, H-2″), 3.90 and 3.85 (6H, 2s, 7-OMe, 4′-OMe), 3.42 (2H, d, 8.0 Hz, H-1″), 1.76 and 1.68 (6H, 2s, H-4″ and -5″); ^{13}C nmr (22.5 MHz, $CDCl_3$/DMSO-d_6) δ 176.0 (C-4), 164.9 (C-7), 160.4 (C-5), 156.0 (C-9), 149.5 (C-4′), 146.7 (C-2), 146.2 (C-3′), 136.2 (C-3), 130.5 (C-1″), 123.2 (C-1′), 122.4 (C-2″), 119.7 (C-6′), 114.7 (C-2′), 114.5 (C-5′), 110.2 (C-6), 103.5 (C-10), 94.8 (C-8), 56.2 (2 × OMe), 25.5 (Me), 21.2 (C-3″), 17.7 (Me).

Triacetate of **2**.—Mp 115°; eims (rel. int.) *m/z* $[M]^+$ 524 (15), 482 (40), 440 (70), 398 (100); ^1H nmr (300 MHz, $CDCl_3$) δ 7.70 (1H, dd, 8.5 and 2 Hz, H-6′), 7.52 (1H, d, 2 Hz, H-2′), 7.05 (1H, d, 8.5 Hz, H-5′), 6.59 (1H, s, H-8), 5.19 (1H, br t, 8.0 Hz, H-2″), 3.90 and 3.88 (6H, 2s, 7-OMe and 4′-OMe), 3.59 (2H, d, 8.0 Hz, H-1″), 2.45–2.35 (9H, br s, OAc × 3), 1.72 (6H, s, H-4″ and -5″).

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