TWO NEW PRENYLATED FLAVONOIDS FROM PARACALYX SCARIOSA

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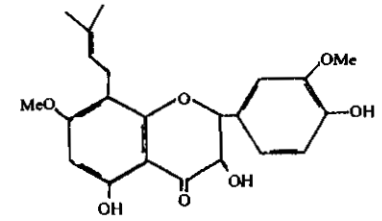
ABSTRACT: *Two new prenylated flavonoids, named scariosin (1) and isorhynchospermin (2) were isolated from the leaves of Paracalyx scariosa together with kaempferol, quercetin, kaempferol 3-O- rutinoside and rutin. The structures of (1) and (2) were characterized as 8-C- prenyl- taxifolin 7, 3'- dimethylether and 6-C-prenylquercetin 7,4'- dimethylether by their chemical and spectral data, respectively.*

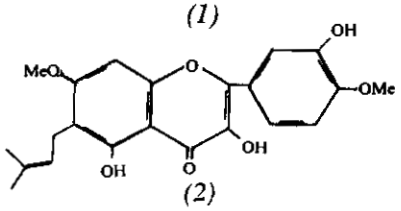
KEY WORDS : *Flavonoids from paracalyx scariosa, Scariosin, Isorhynchospermin, Kaempferol, Quercetin, Kaemferol 3-O-rutinoside, Rutin.*

INTRODUCTION :

Paracalyx scariosa [1] Roxb.(Leguminosae)is the only species of this genus that grows in India and has not been chemically investigated so far. We have examined the leaves of **P. scariosa** and in this paper we report the isolation and characteri- zation of one new prenylated dihydroflavonol, scariosin *(1)* a new prenylated flavonol iso- rhynchospermin *(2)* , as well as the isolation of kaempferol, quercetin, kaempferol 3-O- rutinoside and rutine.



(1)



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EXPERIMENTAL :

Instrumentation

Mass spectra were obtained on a VG Instruments VG- 70 instrument in ei mode at 70 eV. IR spectra were run on a Beckman Model 4244 instrument using KBr pellets. UV spectra on a Beckman 25 spectrophotometer. All NMR experiments were performed on a 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).

solvents for chromatography

All solvents used for chromatography were purchased from Glaxco company and were labeled for chromatography purposes.

Plant materials

P. Scariosa were collected in the month of November from Araku valley, Andhra pradesh, south India.

Methods

Shade dried leaves of P. scariosa (1.5 Kg) were soxhleted with petroleum ether, C_6H_6 and Me_2CO. Concentration of the petrol extract under reduced pressure gave a greenish yellow residue (3.5 g). It was taken in MeOH (100 ml) and was kept in freezer overnight. The sparingly soluble waxes which separated was 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 silica gel (50 g) packed in petroleum ether, petroleum ether/ C_6H_6 mixtures, C_6H_6, C_6H_6/ $CHCl_3$ mixtures, $CHCl_3$/ EtOAc mixtures.

We used (V/V 1:1) for each solvent combination. 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 colourless needles of scariosin *(1)*.

The pale yellow solid (140 mg) obtained from C_6H_6 extract was macerated with 150 ml of MeOH and filtered. Preliminary TLC examination (silica gel G; C_6H_6- dioxane - HOAc; 90: 25: 4V/V) of MeOH soluble part showed two spots with $R_f$values 0.92 (major) and 0.82 (trace). By using preparative TLC, and MeOH as eluent, the major component was obtained as yellow solid which on repeated crystallization from MeOH yielded yellow needles (130 mg) of isorhyncospermin *(2)*.

The Et_2O soluble fractions of Me_2CO extract on further purification by preparative paper chromatography [whatman No. 3, descending, TBA (t- BuOH - HOAc- H_2O), 3:1:1 V/V 30; 18hr] gave kaempferol (80 mg) and quercetin (100 mg).

The EtOAc soluble fraction on concentration gave a yellow solid which was found to be a mixture of two components. By preparative PC using TBA (3:1:1) they gave kamepferol 3-O-rutinoside (45 mg) and rutin (40 mg), respectively.

RESULTS :

Scariosin (1)

Mp 190°; $C_{22}H_{24}O_7$; $[\alpha]_D^{25}$ + 55.4° (c=1.2, py);
UV:λ_{max} (MeOH) (log ε) 290 (4.15), 342 (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 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);
^{1}HNMR:(300 MHz, DMSO- d_6) δ12.08 (1H, br. s, OH- 5: exchangeable in D_2O), 9.12 (1H, br. s, OH-4': exchangeable in D_2O), 7.23 (1H, d,2.5 Hz, H-2'), 7.05 (1H, dd, 8.5 & 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 Hz OH-3), 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, OMe-7), 3.82 (3H, s, OMe-3'), 3.10 (2H, d, 8 Hz, H-1"), 1.55 (6H, m, H-4" & H-5").

Triacetate of (1)
Mp 89°;
^{1}HNMR:(300 MHz, $CDCl_3$) δ7.20 - 7.45 (2H, m, H-6′ & 2′), 6.98 (1H, d, 8.5 Hz, H-5′), 6.30 (1H, s, H-6), 5.62 (1H, d, 12Hz, H-2), 5.25 (1H, d, 12 Hz, H-3), 5.08 (1H, m, H-2"), 3.93 (6H, s, OMe-3′ & 7), 3.25 (2H, d, 8 Hz, H-1"), 2.35 (3H, s, OAc-5), 2.33 (3H, s, OAc-4′), 2.05 (3H, s, OAc-3), 1.62 & 1.55 (6H, 2s, H-4" & 5").

Isorhynchospermin (2)
Mp 190°; $C_{22}H_{22}O_7$;
UV:λ_{max} (MeOH) (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 m/z:$[M]^+$, 398 (100), 383 (84), 369 (6), 368 (3), 367 (3), 343 (11), 330 (45), 315 (6), 179 (6) and 151 (14);
^{1}HNMR:(300 MHz, DMSO - d_6) δ12.50 (1H, s, OH-5), 7.76 (1H, dd, 8.0 & 2.5 Hz, H-6′),7.70 (1H, d, 2.5 Hz, H-2′) 7.10 (1H, d, 8 Hz, H-5′), 6.8 (1H, s, H-8), 5.15 (1H, m, H-2"), 3.90 & 3.85 (6H, 2s, OMe - 7, 4′), 3.42 (2H, d, 8 Hz, H-1") 1.76 & 1.68 (6H, 2s, H-4" & 5");
^{13}CNMR:(22.15 MHz, $CDCl_3$ + DMSO - d_6) 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 (OMe), 25.5 (Me), 21.2 (C - 3") and 17.7 (Me).

Triacetate Of (2)
Mp. 115°;
^{1}HNMR (300 MHz, $CDCl_3$) δ7.70 (1H, dd, 8.5 & 2 Hz, H-6′), 7.72 (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 Hz, H-2"), 3.90 & 3.88 (6H, s, OMe-7 & 4′), 3.59 (2H, d, 8 Hz, H-1"), 2.45 - 2.35 (9H, s, OAcx3), 1.72 (6H, s, H-4", 5").

DISCUSSION :

The petroleum ether extract of **P.scariosa** was column chromatographed over silica gel to yield scariosin *(1)* $C_{22}H_{24}O_7$. Its colour reactions and UV spectrum resembled that of a dihydroflavonol [2a] with λ_{max} (MeOH) at 290 and an inflection at 342 nm. The IR spectrum exhibited absorptions at 3425 (chelated hydroxyl), 1680 (conjugated carbonyl) and 1360 cm^{-1} (gemdimethyl). The ^{1}H NMR spectrum of *(1)* exhibited the typical AB system due to C - 2 and C - 3 protons of dihydroflavonol [2b] at δ5.05 (d, J=11 Hz) and 4.52 (d, J=11 Hz), recpectively. The latter signal was split further due to coupling with OH proton at C - 3 (J = 6 Hz) and found as a doublet at δ5.78. The presence of C - linked prenyl residue [3, 4] in scariosin *(1)* was evidenced from the signals at δ5.10 (vinyl proton), 3.10 (allylic protons) and 1.55 (vinyl methyls). Two three - proton singlet at δ3.90 and 3.82 showed the presence of two methoxy groups and the former was assigned to 7- position based on the fact that there was no bathochromic shift of the UV absorption maximum with NaOAc. A broad signal at δ12.08 was assignd to chelated hydroxyl at C - 5. The presence of three hydroxyl groups in *(1)* was evidenced by the formation of a triacetate ($C_{28}H_{30}O_{10}$). The appearance of H-2′ doublet (δ7.23) 0.18 ppm downfield from the H-6′ doublet (δ7.05) supported B ring with a 3′- methoxy and 4′- hydroxyl substitution pattern [2c]. The downfield shift of the signal for the aromatic singlet of ring A upon acetylation [5] and a batho- chromic shift of 25 nm in the UV spectrum after the addition of $AlCl_3$ [2d] indicated that it must be ortho to the C - 5 hydroxyl. Thus the prenyl residue in scariosin [6] was shown to be located at C - 8 position. A trans orientation of the C- ring methine protons was infered from the large J value (11 Hz) which is typical of diaxial coupling [2b]. Positive optical rotation of *(1)* indicates 2R, 3R-configuration and thus the structure of scariosin

(1) was established as (+) - (2R, 3R)-8-C-prenyltaxifolin 7, 3'- dimethylether. Confirmation of this structure was obtained from the mass spectrum 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 hdyrogen transfer showed one hydroxyl, one methoxy and an isoprenyl group in ring A and a methoxy and hydroxyl in ring B, respectively.

Isorhynchospermin *(2)* isomeric with rhynchospermin [7] was obtained as yellow needles from MeOH soluble part of C_6H_6 extract by preparative TLC. The UV absorption data of the compound were similar to those of a flavonol. A bathochromic shift of 60 nm with $AlCl_3$ reagent clearly showed the presence of a free 3- OH group. The 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 δ3.90 and 3.85 indicating two methoxy groups. The presence of a C- linked prenyl residue was inferred from the signals at δ1.68, 1.76, 3.42 and 5.15. The A- ring aromatic proton appearing as a singlet at δ6.58 was assigned to C- 8 proton on the basis of comparison with the chemical shift value of δ6.41 exhibited by C- 6 proton of rhynchosperimin [7]. The signal due to the H-2' proton in the acetylated compound appeared at δ7.52 slightly higher field than the H-6' proton signal at δ7.70. This behaviour is characteristic for a flavonol containing 4'- methoxy - 3- hydroxyl substitution [8]. Thus isorhynchospermin *(2)* appears to be a C- prenylated omboin constaining two methoxy groups at the 4' and 7- positions and the prenyl residue at the 6- position. The mass spectrum of *(2)* gave the molecular ion peak at m/z 398 and fragments at m/z 179 and 151 which confirms the presence of prenyl group in the A- ring, and confirmed the structure as 6- C- prenyl- quercetin 7, 4'- dimethylether *(2)*. This proposal was in agreement with the ^{13}C-NMR spectral data. The compound was showe to be identical in all respects with the sample of the dehydroderivative of isotirumalin obtained from Rhynchosia cyano- sperma [9].

The acetone extract on solvent fractionation followed by preparative paper chromatography gave kaempferol, quercetine, kaempferol 3-O-rutinoside and rutin.

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