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# RHYNCHOSPERMIN, A PRENYLATED FLAVONOL FROM *RHYNCHOSIA CYANOSPERMA*

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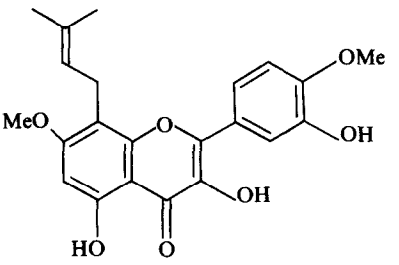
**Key Word Index**—*Rhynchosia cyanosperma*; Leguminosae; prenylated flavonol; rhynchospermin.

**Abstract**—A new flavonol has been isolated from the leaves of *Rhynchosia cyanosperma* and identified as 8-*C*-prenylquercetin 7,4′-dimethyl ether (rhynchospermin).

An earlier paper on the leaves of *Rhynchosia cyanosperma* Benth. reported the presence of tirumalin, rutin, kaempferol-3-rutinoside and pinitol [1]. The methanol-soluble part of the petrol extract by preparative TLC yielded rhynchospermin. The UV absorption data of the compound were similar to those of a flavonol. A bathochromic shift of 62 nm with $AlCl_3$ reagent 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 NMR spectrum exhibited two singlets at $\delta$ 3.98 and 3.93 ppm indicating two methoxyl groups. The benzylic proton of the $\gamma,\gamma$-dimethyl allyl group gave rise to a doublet at $\delta$ 3.54 ppm, while the olefinic proton appeared as a broad multiplet around 5.21 ppm. The presence of a *C*-linked prenyl residue was inferred from the signals at $\delta$ 1.68, 1.82, 3.54 and 5.21 ppm. Of the aromatic protons, H-6 appeared as a singlet at $\delta$ 6.41 ppm which in the triacetyl derivative of the compound appeared as a singlet at $\delta$ 6.65 ppm. The observed downfield shift of 0.24 ppm is consistent with the proton being at C-6 [2]. The signal due to the H-2′ proton in the acetylated compound appeared at $\delta$ 7.54 ppm and at a slightly higher field than the H-6′ proton signal at $\delta$ 7.74 ppm. This behaviour is characteristic for flavonoids containing 4′-methoxy-3′-hydroxy substitution [3]. Thus rhynchospermin appeared to be a *C*-prenylated ombuin containing two methoxyl groups at the 4′ and 7-positions and the prenyl residue at the 8-position. The mass spectrum of the compound gave the molecular ion peak at *m/z* 398 and fragments at *m/z* 151 and 179 which located the prenyl group on the A-ring, and confirmed the structure as 8-*C*-prenylquercetin 7,4′-dimethyl ether (**1**). This proposal was in agreement with the $^{13}C$ NMR data. The compound was shown to be identical in all respects with a sample of the dehydro derivative of 2*R*:3*R*-8-*C*-prenyltaxifolin 7,4′-dimethyl ether (tirumalin) obtained by the iodine oxidation method [4].




**1**

## EXPERIMENTAL

The shade-dried leaves of *Rhynchosia cyanosperma* (0.8 kg) were Soxhlet extracted with hot petrol (bp 60–80°). The petrol extract on concn yielded tirumalin. The mother liquor was dried, macerated with 150 ml MeOH and filtered. The methanol-soluble part obtained by preparative TLC (Si gel $C_6H_6$–$CHCl_3$, 2:3) gave rhynchospermin as a yellow, amorphous powder (30 mg, 0.0037%).

*Rhynchospermin* (**1**). Yellow, amorphous powder, mp 216–218° (MeOH), $C_{22}H_{22}O_7$ (398.40). Found: C, 66.10; H, 5.24; calc.: C, 66.32; H, 5.57%. It gave a green colour with alcoholic $FeCl_3$, brick red with diazotized sulphanilic acid and an initial pink colour changing to red with Mg–HCl. $R_f$ values were 0.91 (PC, BAW, 4:1:5), 0.00 (PC, 15% aq. HOAc) and 0.90 (TLC, Si gel $C_6H_6$–dioxane–HOAc, 90:25:4). UV $\lambda_{max}$ nm (MeOH): 256,272 sh, 310 sh, 338 sh, 380 (log $\varepsilon$ respectively 4.41, 4.28, 3.98, 4.06, 4.30); + $AlCl_3$; 268, 310 sh, 365, 442; + $AlCl_3$/HCl; 268, 280 sh, 310, 363, 440; + NaOAc; 272, 335 br, 419; + NaOAc/$H_3BO_3$; 260, 275 sh, 335 sh, 380; + NaOMe; 266, 345 sh, 429. IR (KBr) $cm^{-1}$: 3535, 3356 (OH), 1655 (C=O), 1260 (C–O), 800 (Ar). $^1H$ NMR (60 MHz, $CDCl_3$, DMSO-$d_6$, TMS as int. standard): $\delta$ 7.72 ppm (*m*, 2 H, H-2′, H-6); 6.96 (*d*, $J$ = 8.5 Hz, 1 H, H-5′); 6.90 (*br*, 1 H, OH-3′); 6.41 (*s*, 1 H, H-6); 5.21 (*m*, 1 H, $\beta$CH=); 3.98, 3.93 (*s*, 6 H, OMe); 3.54 (*d*, $J$ = 8 Hz, 2 H, $\alpha CH_2$); 1.82, 1.68 (*s* (*br*), 6 H, $\gamma$-Me); 11.80 (*br*, 1 H, OH-5). MS *m/z* 398 $M^+$ (70% rel. int): 383 (100), 368 (5.8), 367 (6.3), 343 (10.3), 330 (50.1), 315 (11.1), 179 (3.6), 151 (18.3). $^{13}C$ NMR (20.15 MHz, $CDCl_3$ + DMSO-$d_6$, TMS as int. standard): $\delta$ 175.9 C-4, 171.8 C-7, 159.2 C-5, 156.0 C-9, 150.9 C-4′, 148.9 C-2, 145.8 C-3′, 136.9 C-3, 132.5 C-$\gamma$, 124.5 C-1, 122.3 C-$\beta$, 120.9 C-6′, 114.7 C-2′, 110.8 C-5′, 108.2 C-8, 103.5 C-10, 94.6 C-6, 56.1 OMe, 25.7 Me 21.7 $CH_2$-$\alpha$; 17.9 Me.

*Rhynchospermin triacetate*. $M^+$ 524. $^1H$ NMR ($CDCl_3$, TMS as int. standard): $\delta$ 7.74 ppm (*dd*, $J$ = 8.5 and 2 Hz, 1 H, H-6′);

7.54 (*d*, $J$ = 2 Hz, 1 H, H-2′); 7.07 (*d*, $J$ = 8.5 Hz, 1 H, H-5′); 6.65 (*s*, 1 H, H-6); 5.19 (*t* (*br*), $J$ = 8 Hz, 1 H, βCH=); 3.92, 3.90 (*s*, 6 H, OMe); 3.59 (*d*, $J$ = 8 Hz, 2 H, $\alpha CH_2$), 2.47, 2.34 (*s*, 9 H, OAc); 1.74 (*s* (*br*) 6 H, γ-Me).

*Conversion of tirumalin to the corresponding flavonol by the iodine oxidation method* [4]. Tirumalin (10 mg), fused KOAc (60 mg) and HOAc (0.6 ml) were heated under reflux and to the boiling soln was added during the course of an hour a soln of $I_2$ (10 mg) in HOAc (0.4 ml). The mixture was refluxed for 3 hr, after which most of the acetic acid was removed under red. pres. and the residue treated with water satd with $SO_2$ (2 ml). The brownish yellow solid (4 mg) obtained was crystallized from MeOH to yield the dehydro derivative of tirumalin as a yellow solid. It agreed in all respects with the natural sample of rhynchospermin.

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# ALKALOIDS AND FLAVONOIDS OF *MELICOPE INDICA*

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**Key Word Index**—*Melicope indica*; Rutaceae; 2-quinolone; *N*-methylatanine; furoquinolines; dictamnine; evolitrine; flavones; meliternatin; melibentin; 3,5,8-trimethoxy-6,7: 3′,4′-dimethylenedioxyflavone.

**Abstract**—The following substances were isolated from the leaves of *Melicope indica*: *N*-methylatanine, dictamnine, evolitrine, meliternatin, melibentin and a new flavonoid which was shown to be 3,5,8-trimethoxy-6,7: 3′,4′-dimethylenedioxyflavone by its spectroscopic properties.

*Melicope indica* Wight is a shrubby Rutaceae which seems to be endemic of south Indian hills, at elevations of about 2200 m. This is the only one of the genus *Melicope* known in peninsular India and is apparently unused in traditional medicine. As far as we know, no phytochemical research has been carried out on *Melicope indica*. A voucher specimen (Blasco No. 1280) has been deposited at the Institut de la Carte Internationale du Tapis Végétal, 31400 Toulouse, France. Its identification has been confirmed by Dr. B. C. Stone, University of Malaya, Kuala Lumpur, who is an authority on Asiatic Rutaceae.

Three alkaloids (A, B and E) and three flavonoids (C, D and F) were extracted from the leaves by column chromatography using silica gel and alumina, and silica gel PC.

The UV spectrum of A was characteristic of a 2-quinolone [1] and was confirmed by the absence of a shift in the presence of HCl [2] and by the presence of an important peak near 1640 $cm^{-1}$ in the IR spectrum. The $^1H$ NMR spectrum indicated the presence of four aromatic protons at C-6, C-7, C-8 (between $\delta$ 7.17 and 7.42) and C-5 ($\delta$ 7.73), also indicating a 2-quinolone. The mass spectrum showed the presence of an aliphatic chain [3]. This compound was identified as a *N*-methylatanine by spectral comparison with data of a known standard. This alkaloid has already been isolated from at least two other woody plants, *Almeidea guyanensis* (Rutaceae) [4]