BAKUCHICIN, A NEW SIMPLE FURANOCOUMARIN FROM PSORALEA CORYLIFOLIA L.

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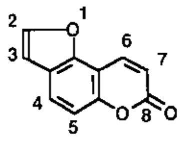
Abstract —— A new simple furanocoumarin, bakuchicin, has been isolated from the hexane-extract of seeds of Psoralea corylifolia L. (Leguminosae) alone with stigmasterol, psoralen and bakuchiol. The structure of bakuchicin has been shown as 8-oxo-8H-furo[2,3-f][1]benzopyran (**1**) by spectral means.

The seeds of Psoralea corylifolia L. (Leguminosae, Sanskrit name: Bakuchin) is used as a tonic or an aphrodisiac against impotence and menstruation disorders. The seed-oil of this plant also is used externally for the treatment of leucodermy, psoriasis, and leprosy in Indian folkloric remedy.[1] Many studies on the constituents of the seeds have been reported.[2] Now the presence of a new simple furanocoumarin was proved.

The n-hexane extract of the powdered seeds of P. corylifolia yielded an oily fraction which on silica gel chromatography gave a 0.1% of yield of a crystalline component (**1**), mp 138 °C, besides the known compounds, stigmasterol, psoralen (**2**), and bakuchiol (**3**). **1** is a new compound, for which we propose the name bakuchicin.



1

	δ (ppm)	J (Hz)
C2-H	7.70 (d)	2.0
C3-H	7.14 (dd)	2.0,1.25
C4-H	4.44 (dd)	8.75,1.25
C5-H	7.38 (d)	8.75
C6-H	7.82 (d)	9.5
C7-H	6.40 (d)	9.5

Table 1. ^{1}H Nmr spectral data of **1**

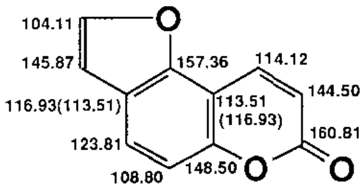
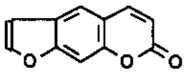


Figure 1. ^{13}C Nmr spectral data of **1**



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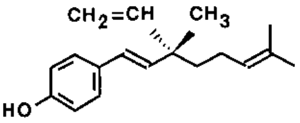

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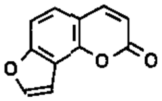

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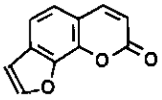

1a

Bakuchicin (**1**) analyzed for $C_{11}H_6O_3$, a formula which confirmed by high-resolution mass spectrum molecular ion peak 186.0334 (Calcd 186.0317). The ultraviolet absorption spectrum (in 95% EtOH) showed maxima at 242 nm (infl.) (log ε 4.47), 248 nm (log ε 4.48) and 297 nm (log ε 4.13), while the infrared spectrum (in $CHCl_3$) displayed bands at 1722 and 1619 cm^{-1}, suggesting the presence of a furanocoumarin skeleton. This suggestion is supported by spectral data of ^1H nmr (Table 1), ^{13}C nmr (Figure 1), and 2D nmr.

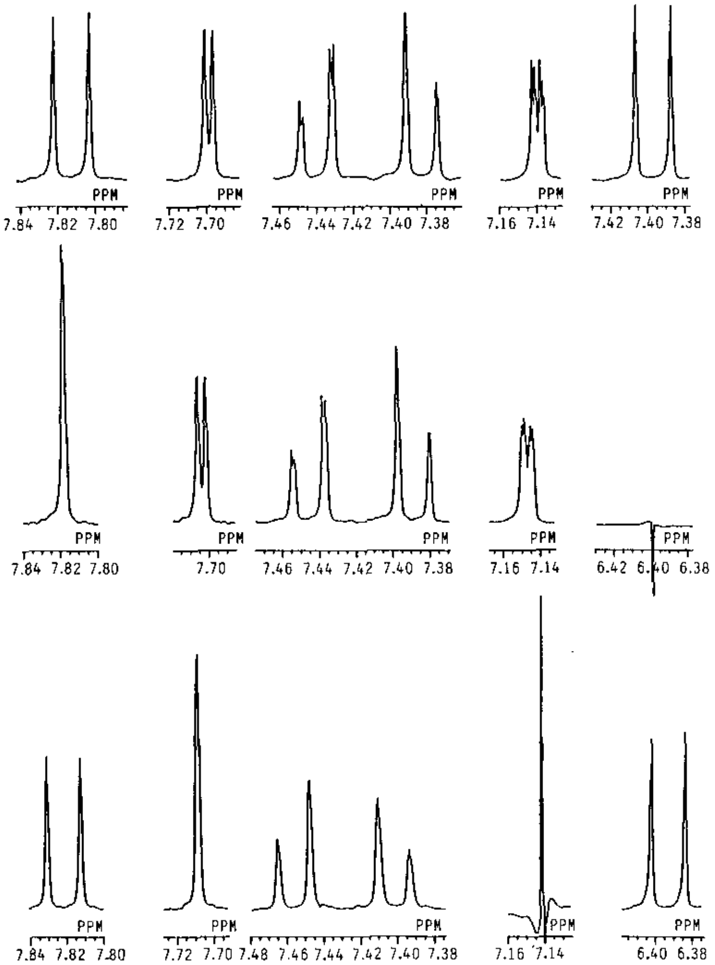

Figure 2. Double resonance ^1H nmr spectra of **1**

The COSY spectrum of bakuchicin showed that the signal at δ 7.14 (1H, dd, J=2.0 Hz, 1.25 Hz) is correlated with the signals at δ 7.44 (1H, dd, J=8.75 Hz, 1.25 Hz) and δ 7.70 (1H, d, J=2.0 Hz), but no correlation between the signals δ 7.82 and other aromatic protons. These findings, combined with a double-resonance experiment (Figure 2), showed that another structure (**1a**) can be ruled out and the structure of bakuchicin is elucidated as 8-oxo-8H-furo[2,3-f][1]benzopyran (**1**). Interestingly, previous investigators have been reported isolation of angelicin (**4**) from seeds of P. corylifolia,[3] however, we proved the presence of bakuchicin (**1**), a new isomeric simple furanocoumarin, in this paper.

EXPERIMENTAL

Melting points were taken on a Yamato MP-2 melting point apparatus and are uncorrected. Ultraviolet spectra were recorded with a Hitachi U-3200 spectropohotometer. Infrared spectra were determined as $CHCl_3$ solutions on a Jasco A-100S infrared spectrophotometer. ^{1}H Nmr and ^{13}C nmr spectra were recorded in $CDCl_3$ on a JEOL FX-500 spectrometer. TMS was used as an internal standard; chemical shifts are reported in δ ppm units. Mass spectra were determined with a JEOL DX-303 double focusing mass spectrometer operating at 70 eV.

Isolation of substances Dried and powdered seeds of P. corylifolia (1000 g) were exhaustively extracted with n-hexane (2 l x 4) at room temperature for 24 h. The n-hexane solution was evapolated and then subjected to column chromatography on silica gel (6 x 50 cm). Elution was accomplished with n-hexane and increasing quantities of AcOEt. Fractions of about 50 ml were collected and monitored by thin-layer chromatography (tlc). The four major compounds, bakuchiol **3** (52.127 g), stigmasterol (0.050 g), bakuchicin **1** (0.992 g), and psoralen **2** (0.884 g), were obtained from the corresponding fractions 10-16, 28-30, 31-35, and 37-41, respectively.

Bakuchiol (3) Colorless oil, bp 146-147 °C/0.8 mmHg. Ms m/z: 256 (M^+) (Calcd 256). The identity of this compound was established by comparison of ^{1}H nmr spectral data.[4] Bakuchiol 3,5-dinitrobenzoate: Pale yellow plates (acetone-MeOH), mp 130 °C (lif.,[4] mp 136 °C). Anal. Calcd for $C_{25}H_{26}N_2O_6$: C, 66.56; H, 5.82; N, 6.22. Found: C, 66.61; H, 5.97; N, 6.14. Fdms m/z: 450 (M^+).

Stigmasterol Colorless plates (MeOH), mp 170 °C. Anal. Calcd for $C_{29}H_{48}O$: C, 84.40; H, 11.72. Found: C, 84.59; H, 11.77. Ms m/z: 412 (M^+).

Bakuchicin (1) Colorless needles (acetone-n-hexane), mp 138 °C. Anal. Calcd for

$C_{11}H_6O_3$: C, 70.97; H, 3.25. Found: C, 70.97; H, 3.46. Ms *m/z*: 186.0334 (Calcd 186.0317). Ir ($CHCl_3$) cm^{-1}: 1722 (α,β-unsaturated lactone), 1619 (aromatic). Uv (95% EtOH) nm (log ε): 242 infl. (4.47), 248 (4.48), 297 (4.13). ^1H Nmr: Table 1. ^{13}C Nmr: Figure 1.

Psoralen (2) Colorless needles (MeOH), mp 155 °C. Anal. Calcd for $C_{11}H_6O_3$: C, 70.97; H, 3.25. Found: C, 71.11; H, 3.29. Ms *m/z*: 186 (M^+). The identity of this compound with an authentic sample of psoralen was confirmed by comparison of ^1H nmr, ir, uv spectra, and tlc behavior.

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