

## Note

### New constituents from *Psoralea corylifolia*

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Two new metabolites, named psoralester **1** and psorachromene **2**, a *trans* isomer of bavachromene together with five known compounds have been isolated from the seeds of *Psoralea corylifolia* L. and characterized on the basis of their detailed NMR and mass spectral data. Psoralester possess a ten-membered lactone moiety and a long chain ester.

**Keywords:** Psoralester, lipid diester, psorachromene, chalcone, *Psoralea corylifolia* L., Fabaceae,

*Psoralea corylifolia* L., (Fabaceae), commonly known as Bakuchi in Sanskrit and Babchi in Hindi is reported to be grown in Rajasthan and eastern district of Punjab adjoining Uttar Pradesh for its seeds. The seeds are used in indigenous medicines. They have been specially recommended in the treatment of leucoderma, leprosy, psoriasis and inflammatory diseases of the skin and are prescribed both for oral administration and for local application in the form of a paste or ointment<sup>1</sup>. The seed have been reported to have antiseptic properties as well<sup>2</sup>.

Several furanocoumarins, isoflavanoids, chalcones and flavones have been isolated from the seeds of *P. corylifolia*<sup>3-11</sup>, bakuchiol, and psoralen being the major constituents and reported to possess a number of biological properties<sup>11,12</sup>.

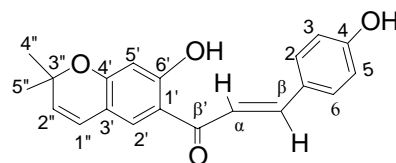
In the present communication, we describe the isolation and structural elucidation of psoralester **1** and psorachromene **2** as new compounds along with known compounds, bakuchiol, bakuchicin, psoralen, corylin and 7-methoxy-bavachin.

### Results and Discussion

The compound **1** was obtained as a viscous liquid with molecular ion peaks at  $m/z$  366 in the EIMS,  $m/z$  367  $[M+H]^+$  in the FABMS corresponding to molecular formula  $C_{22}H_{38}O_4$ . The IR spectrum of the

compound showed ester carbonyls and ( $1741$ ,  $1735$   $cm^{-1}$ ) and 1, 2 disubstituted *cis* double bond ( $1630$ ,  $670$   $cm^{-1}$ , ref. 13). NMR assignments for all  $^1H$  and  $^{13}C$  resonances, position and stereochemistry of groups in the compound were made by the analysis of  $^1H$ ,  $^{13}C$ , DEPT, COSY and HETCOR experiments (**Table I**). The  $^1H$ ,  $^{13}C$  and DEPT spectra gave the presence of one *cis* double bond ( $w/2 = 5.9$  and  $6.2$  Hz for the olefinic protons), one oxymethylene, one oxymethine, two ester carbonyls, fifteen methylenes and one methyl groups. In the  $^1H$  and COSY spectrum, a multiplet at  $\delta$  5.19, correlating with the ester oxymethylene protons ( $H_2-9$ ) double doublets at  $\delta$  4.07 and 4.22 and another multiplet at  $\delta$  5.26, correlating with  $H_2-6$  protons multiplet at  $\delta$  1.98 were assigned for the H-8 and H-7 olefinic protons respectively. A broad triplet,  $J = 5.4$  Hz at  $\delta$  3.9 showing correlation with  $H_2-3$ ,  $H_2-5$  protons multiplet at  $\delta$  1.60 was assigned for oxymethine proton (H-4) and its coupling constant (5.4 Hz) indicated  $\alpha$ -orientation of the second ester moiety. Correlations between the  $H_2-2$  and  $H_2-2'$  protons with  $H_2-3$  and  $H_2-3'$  protons respectively suggested a ten-membered cyclic ester moiety and a second ester group is present in the compound. In the EIMS of the compound **1**, characteristic ions at  $m/z$  301(**a**), 65(**b**), 197(**c**), the base peak at  $m/z$  104(**d**), 212, 154, generated through Maclafferty rearrangement, an  $\alpha$ -fission at C-3 ester function with  $\gamma$  hydrogen transfer and a series of significant ions usually occurring for an acyclic ester<sup>14</sup> (**Figure 1**) further supported the ten member cyclic ester with a double bond, attached to a  $C_{13}$  acyclic ester. Significant correlations observed in the HETCOR, shown by arrows on the structure of **1** (**Figure 2**), supported the structure and named it psoralester.

Compound **2**, m.p.  $212-13^\circ C$  was obtained as red crystals from the chloroform fraction of the seeds of the plant. It was analyzed for molecular formula



**Table I** — NMR assignments for psoralester **1** (in CDCl<sub>3</sub>, 300/75MHz)

H/C	$\delta_H$	$\delta_C$	DEPT	<sup>1</sup> H- <sup>1</sup> H COSY	HMBC
1		173.3	C	—	—
2	2.27 (t, 7.2)	34.0 <sup>a</sup>	CH <sub>2</sub>	H <sub>2</sub> -3	C-1, C-3, C-4
3	1.60 (m)	29.0 <sup>b</sup>	CH <sub>2</sub>	H <sub>2</sub> -2, H-4	C-1, C-2
4	3.9 (br t, 5.4)	68.9	CH	H <sub>2</sub> -3, H <sub>2</sub> -5	C-1'
5	1.60(m)	27.1	CH <sub>2</sub>	H-4, H <sub>2</sub> -6	C-7
6	1.98(m)	29.2 <sup>b</sup>	CH <sub>2</sub>	H <sub>2</sub> -5, H-7	C-4
7	5.26 (m, w/2=5.9)	130.0	CH	H <sub>2</sub> -6, H-8	C-9
8	5.19 (m, w/2=6.2)	129.7	CH	H-7, H <sub>2</sub> -9	C-7
9a	4.07 (dd, 11.4, 5.8)	62.1	CH <sub>2</sub>	H-8	C-1, C-7
9b	4.22 (dd, 11.4, 5.8)				
1'		172.8	C	—	—
2'	2.27 (t, 7.2)	34.2 <sup>a</sup>	CH <sub>2</sub>	H <sub>2</sub> -3'	C-1', C-3'
3'	1.60 (m)	24.8 <sup>c</sup>	CH <sub>2</sub>	H <sub>2</sub> -2', H <sub>2</sub> -4-12'	C-1', C-2'
4'-10'	1.18 (br s)	24.6 <sup>c</sup>	CH <sub>2</sub>		
		29.3 <sup>b</sup>	CH <sub>2</sub>		
		29.4 <sup>b</sup>	CH <sub>2</sub>		
		29.5 <sup>b</sup>	CH <sub>2</sub>	H <sub>2</sub> -3', H <sub>3</sub> -13'	—
		29.6 <sup>b</sup>	3×CH <sub>2</sub>		
11'	1.18 (br s)	31.8	CH <sub>2</sub>		
12'	1.18 (br s)	22.6	CH <sub>2</sub>		
13'	0.80 (t, 6.2)	14.1	CH <sub>3</sub>	H <sub>2</sub> -4'-12'	C-11', C-12'

Coupling constants (*J*) parentheses,  
a, b, c = signals interchangeable

C<sub>20</sub>H<sub>18</sub>O<sub>4</sub> by [M+H]<sup>+</sup> ion at *m/z* 323 in its FAB-MS and NMR data. The UV-Vis absorption bands at  $\lambda_{\max}$  260 and 365 were suggestive for a chalcone skeleton<sup>15</sup>. Its IR spectrum showed characteristic absorptions for chalcone carbonyl (1638 cm<sup>-1</sup>), *gem* dimethyl group and a *para* substituted benzene ring. The <sup>1</sup>H NMR spectrum exhibited a sharp singlet at  $\delta$  1.42 for *gem* dimethyl group (H<sub>3</sub>-4'', H<sub>3</sub>-5''), two doublets, *J* = 9.0 Hz, at  $\delta$  6.40 and 5.62 for two olefinic protons (H-1'', H-2'') of the chromene ring, two *ortho* coupled doublets, *J* = 8.4 Hz centered at  $\delta$  6.88 and 7.60 integrating for four protons (H-3, H-5 and H-2, H-6), of A<sub>2</sub>B<sub>2</sub> pattern of the phenyl ring, two singlets at  $\delta$  6.27 and 7.72 for C-5' and C-2' protons. All these spectral data are fully consistent with the values reported for bavachromene<sup>4</sup> except instead a  $\alpha/\beta$ - two proton singlet for bavachromene (m.p. 196-97°C) and other chalcones<sup>6-8</sup>, it appears as two doublets at  $\delta$  7.53 and 7.78 with coupling constant (*J*) 15.3 Hz which suggested a *trans* nature of the chalcone **2**. The upfield <sup>13</sup>C chemical shift ( $\delta$  115.6) for the C- $\alpha$  of compound **2**, agreeing with the

chalcones containing *trans* C- $\alpha/\beta$  double bond reported in the literature<sup>16-19</sup>, further supported the structure **2**. It was characterized as psorachromene, the *trans* isomer of bavachromene and is the first report from a natural source.

The known compounds isolated were identified by comparison of their spectral data reported for bakuchiol<sup>10</sup>, bakuchicin and psoralen<sup>9</sup>, corylin<sup>5</sup>, and 7-methoxy-bavachin<sup>3</sup>.

### Experimental Section

Melting points (°C) were uncorrected. IR (KBr/neat) spectra were recorded on a Perkin-Elmer instrument; UV detection was carried at 254 and 366nm on a Pye-Unicam SP8-100 spectrophotometer; NMR: <sup>1</sup>H, <sup>13</sup>C, DEPT-135, <sup>1</sup>H-<sup>1</sup>H COSY and HETCOR spectra were recorded in a Bruker Avance DRX-300 spectrometer using TMS as internal standard, chemical shift  $\delta$ , in ppm and coupling constants *J*, in Hz; EIMS data: 70 eV, recorded on JEOL JMSD-300 spectrometer and FABMS (positive) data, on JEOL SX 102/DA-600. Silica-gel, 60-120

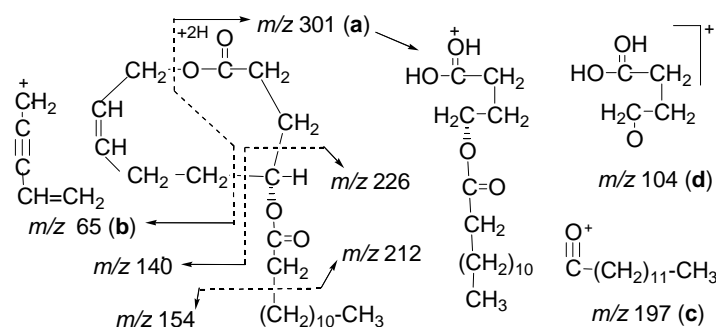
EIMS fragmentations of **1**

Figure 1

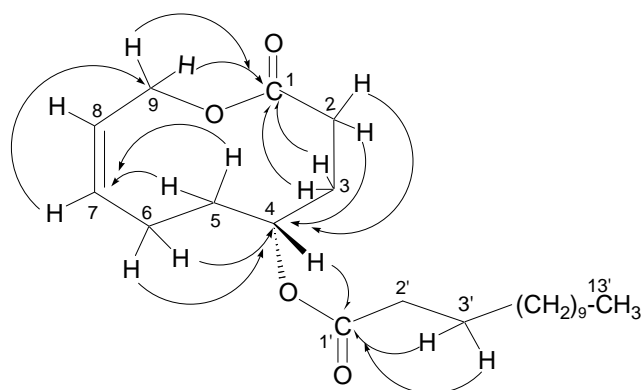
HMBC correlations of **1**

Figure 2

mesh (Merck) was used for CC. TLC was run in silica-gel 60 F<sub>254</sub> pre-coated aluminum plates (0.2 mm, Merck) and spots were developed with glacial AcOH-H<sub>2</sub>SO<sub>4</sub>-anisaldehyde (50:1:0.5) followed by heating at 110°C for 1-2 min.

**Plant material:** The seeds of *Psoralea corylifolia* were purchased from the local market (Lucknow) in the month of December, 2001. The seeds were sown in the experimental farm of CIMAP, Lucknow for its identification. A voucher specimen is deposited in the herbarium of the institute.

**Isolation and identification:** Air-dried and powdered seeds (1.32 kg) of *P. corylifolia* were extracted with MeOH (4 × L) for 48 hr at room temperature. The combined extracts were concentrated and partitioned with chloroform and *n*-butanol. The successive chloroform extractions 4 × 00 mL thus obtained were concentrated and dried under vacuum to furnish brown residue (54 g). A portion of the chloroform extract (40 g) was chromatographed over silica-gel (1.2 kg), eluting with *n*-hexane and increasing the polarity by ethyl acetate and methanol.

Based on their respective TLC profiles, fractions were pooled and concentrated. Prep TLC (*n*-hexane-ethyl acetate, 85:15) of *n*-hexane-ethyl acetate, 90:10 column fractions, 20-32 furnished viscous compound **1**, 0.032 g. Recrystallization of *n*-hexane-ethyl acetate 60:40 fractions, 151-57 with MeOH yielded compound **2**, 0.017g. Re-CC/prep TLC of different mother column fractions furnished five known compounds.

**Psoralester 1:** IR: 1741 and 1737 (ester CO), 1630 and 670 (*cis* double bond), 2920, 2851, 1465, 1358 and 723 cm<sup>-1</sup> (long chain); <sup>1</sup>H NMR, <sup>13</sup>C/DEPT NMR See **Table I**; <sup>1</sup>H-<sup>1</sup>H COSY and HETCOR See **Table I**; FABMS: *m/z* 367[M + H]<sup>+</sup>, EIMS: *m/z* (rel. Int.) 366[M<sup>+</sup>, C<sub>22</sub>H<sub>38</sub>O<sub>4</sub>] (3), 351[M - CH<sub>3</sub>]<sup>+</sup> (12), 340[M - CH=CH]<sup>+</sup> (7), 301[M - b]<sup>+</sup>(C<sub>17</sub>H<sub>33</sub>O<sub>4</sub><sup>+</sup>, a) (54), 269[a-(CH<sub>3</sub>+OH)]<sup>+</sup> (87), 226(C<sub>14</sub>H<sub>26</sub>O<sub>2</sub><sup>+</sup>) (15), 225 [M-C<sub>10</sub>H<sub>21</sub>]<sup>+</sup> (9), 213 (C<sub>13</sub>H<sub>25</sub>O<sub>2</sub><sup>+</sup>) (5), 212 (C<sub>11</sub>H<sub>16</sub>O<sub>4</sub><sup>+</sup>) (11), 210(C<sub>13</sub>H<sub>22</sub>O<sub>2</sub><sup>+</sup>) (13), 197(C<sub>13</sub>H<sub>25</sub>O<sup>+</sup>, c) (11), 169(C<sub>9</sub>H<sub>13</sub>O<sub>3</sub><sup>+</sup> / C<sub>14</sub>H<sub>26</sub>O<sub>2</sub><sup>+</sup>) (15), 155(C<sub>11</sub>H<sub>23</sub><sup>+</sup>) (3), 154(C<sub>11</sub>H<sub>22</sub><sup>+</sup>) (21), 153(C<sub>9</sub>H<sub>13</sub>O<sub>2</sub><sup>+</sup>) (4), 141 ((C<sub>5</sub>H<sub>11</sub>)<sup>+</sup>) (18), 140 (C<sub>8</sub>H<sub>12</sub>O<sub>2</sub><sup>+</sup>) (11), 104 (C<sub>4</sub>H<sub>8</sub>O<sub>3</sub><sup>+</sup>, d) (100), 85 (C<sub>6</sub>H<sub>13</sub><sup>+</sup>) (15), 65(C<sub>5</sub>H<sub>5</sub><sup>+</sup>, b) (17), 57(C<sub>4</sub>H<sub>9</sub><sup>+</sup>) (47), 44 (CO<sub>2</sub>) (72), 43 (C<sub>3</sub>H<sub>7</sub><sup>+</sup>) (27).

**Psorachromene 2:** m.p. 213°C; UV: 206, 260, 365 nm (MeOH); IR (KBr) 3340 (OH), 1638 (chalcone carbonyl), 1552, 1375, 1136 (gem dimethyl), 967(*trans* double bond), 837 cm<sup>-1</sup> (*p*-substituted benzene ring); <sup>1</sup>H NMR (CDCl<sub>3</sub>): 1.42 (6H, s, H<sub>3</sub>-4'', H-5''), 5.62 (1H, d, *J* = 9.0, H-2''), 6.40 (1H, d, *J* = 9.0, H-1''), 6.27 (1H, s, H-5'), 6.88 (2H, d, *J* = 8.4, H-3, H-5), 7.53 (1H, d, *J* = 15.3, H-α), 7.60 (2H, d, *J* = 8.4, H-2, H-6), 7.72 (1H, s, H-2'), 7.78 (1H, d, *J* = 15.3, H-β); <sup>13</sup>C NMR (DEPT), (CDCl<sub>3</sub>): 27.3 (C-4'', C-5''), 76.7 (C-3''), 102.9 (C-5'), 112.3<sup>a</sup>, 112.9<sup>a</sup> (C-1', C-3'), 114.9 (C-3, C-5), 115.6 (C-α), 119.9 (C-1''), 124.7 (C-1), 126.7, 127.4 (C-2', C-2''), 129.6 (C-2, C-6), 143.6 (C-β), 158.9<sup>c</sup> (C-4), 159.3<sup>c</sup> (C-6'), 164.9 (C-4'), 190.5 (C-β'), (a, b, c = signals

interchangeable); FABMS:  $m/z$  323  $[M + H]^+$ ,  $C_{20}H_{18}O_4$ , 307  $[M - CH_3]^+$  (36), 289  $[M - CH_3 - H_2O]^+$  (18), 203  $[M - CH=CHC_6H_4OH]^+$  (11), 120  $[M + H - 203]^+$  (19), 119  $[CH=CHC_6H_4OH]^+$  (17), 107  $[CH_2C_6H_4OH]^+$  (32).

**Bakuchiol:** Pale yellow viscous compound, 1.8 g, EIMS:  $m/z$  256  $[M]^+(C_{18}H_{24}O)$ ;  $^1H$ ,  $^{13}C$  NMR spectral data are in agreement with literature values<sup>10</sup>.

**Bakuchicin:** Colourless needles, 0.165 g (acetone-*n*-hexane), m.p. 138-39°C, EIMS:  $m/z$  186  $[M]^+(C_{11}H_6O_3)$ ;  $^1H$ ,  $^{13}C$  NMR spectral data are in agreement with literature values<sup>9</sup>.

**Psoralen:** Colourless crystals, 0.075 g (MeOH), m.p. 169°C, EIMS:  $m/z$  186  $[M]^+(C_{11}H_6O_3)$ ; IR, UV,  $^1H$  NMR spectral data are in agreement with literature values<sup>9</sup>.

**Corylin:** Colourless crystals (acetone-*n*-hexane), 0.123 g, m.p. 238-39°C, EIMS:  $m/z$  320  $[M]^+C_{20}H_{16}O_4$ ; IR, UV,  $^1H$  NMR spectral data are in agreement with literature values<sup>5</sup>.

**7-Methoxy-bavachin:** Colourless crystals, 0.055 g (acetone-*n*-hexane), m.p. 154-55°C, FABMS (positive):  $m/z$  339  $[M+H]^+$ ,  $C_{21}H_{22}O_4$ ; IR, UV,  $^1H$  NMR spectral data in agreement with literature values<sup>3</sup>.

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