

## 4-Thiazolidinones, Part XX: Thioindigoid Experimental

## Dyes from 3-Aryl-2-arylimino-4-Thiazolidinones and 3-Aryl-2,4-thiazolidinediones

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Manuscript received 25 June 1973; accepted 22 August 1973

PREVIOUS papers in this series<sup>1,2</sup> have shown that the reactive methylene group of the 4-thiazolidinones and thiazolidine-2,4-diones may be condensed with isatin to give thioindigoid dyes. In continuation of our previous work,<sup>1,2</sup> syntheses of several new thioindigoid dyes have been effected.

3-Aryl-2-arylimino-4-thiazolidinones<sup>3</sup> and 3-aryl-2,4-thiazolidinediones<sup>4</sup>, prepared according to the method described previously, were condensed with isatin to obtain the title compounds. In Table 1 are listed in new 5-(2-oxo-3-indolinylidene)-3-aryl-2-arylimino-4-thiazolidinones and in Table 2 are listed the new 5-(2-oxo-3-indolinylidene)-3-aryl-2,4-thiazolidinediones. These dyes dissolve in concd. sulphuric acid producing a red or chocolate-brown colour.

5-(2-Oxo-3-indolinylidene)-3-*o*-fluorophenyl-2-*o*-fluorophenylimino-4-thiazolidinone: A mixture of 3-*o*-fluorophenyl-2-*o*-fluorophenylimino-4-thiazolidinone (6 g.), isatin (3 g.), anhydrous sodium acetate (5 g.) glacial acetic acid (40 ml.) and acetic anhydride (5 ml.) was refluxed in an oil bath at 160° for five hr. After the completion of the reaction (which was indicated by the appearance of dark red precipitate) the reaction mixture was cooled and poured in cold water. The precipitate obtained was collected, washed successively with water, dilute acetic acid and ethanol to give the title compound, m.p. 240°; yield: 6.8 g. (80%).

A number of 5-(2-oxo-3-indolinylidene)-3-aryl-2-arylimino-4-thiazolidinone dyes synthesised by applying the above method are listed in Table 1.

5-(2-Oxo-3-indolinylidene)-3-*p*-fluorophenyl-2,4-thiazolidinedione: A mixture of 3-*p*-fluorophenyl-2,4-thiazolidinedione (1.56 g.), isatin (1 g.), anhydrous sodium acetate (2 g.), glacial acetic acid (15 ml.) and acetic anhydride (2 ml.) was refluxed in an oil bath at 150°-60° for 4 hr. After the completion of the reaction, the reaction mixture was cooled and poured

TABLE 1: 5-(2-OXO-3-INDOLINYLLIDENE)-3-ARYL-2-ARYLIMINO-4-THIAZOLIDINONES

S.No.	Ar. group	m.p. °C	Yield %	Colour	Colour in conc. H <sub>2</sub> SO <sub>4</sub>	Molecular Formula	Analysis %			
							C	H	N	S
1.	<i>o</i> -Fluorophenyl	240	80	Red	Dark brown	C <sub>23</sub> H <sub>13</sub> F <sub>2</sub> N <sub>3</sub> O <sub>2</sub> S	Found 63.92 Calc. 63.74	3.12 3.00	9.45 9.70	7.52 7.39
2.	<i>p</i> -Fluorophenyl	225	82	Orange red	Deep red	C <sub>23</sub> H <sub>13</sub> F <sub>2</sub> N <sub>3</sub> O <sub>2</sub> S	Found 63.48 Calc. 63.74	3.34 3.00	9.98 9.70	7.72 7.39
3.	<i>p</i> -Bromophenyl	222	75	Dark red	Deep red	C <sub>23</sub> H <sub>13</sub> Br <sub>2</sub> N <sub>3</sub> O <sub>2</sub> S	Found 49.38 Calc. 49.73	2.64 2.34	7.86 7.57	5.34 5.77
4.	<i>o</i> -Hydroxyphenyl	218	70	Dark red	Violet red	C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S	Found 64.72 Calc. 64.33	3.66 3.50	9.39 9.79	7.83 7.46
5.	<i>m</i> -Hydroxyphenyl	278	75	Brown	Violet red	C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S	Found 64.68 Calc. 64.33	3.78 3.50	9.55 9.79	7.82 7.46
6.	<i>p</i> -Hydroxyphenyl	236	70	Dark red	Reddish brown	C <sub>23</sub> H <sub>15</sub> N <sub>3</sub> O <sub>4</sub> S	Found 64.66 Calc. 64.33	3.67 3.50	9.49 9.79	7.76 7.46
7.	<i>o</i> -Nitrophenyl	212	60	Dark brown	Blackish red	C <sub>23</sub> H <sub>13</sub> N <sub>6</sub> O <sub>6</sub> S	Found 56.94 Calc. 56.67	2.36 2.67	14.24 14.37	6.38 6.57
8.	<i>m</i> -Nitrophenyl	204	78	Red	Dark red	C <sub>23</sub> H <sub>13</sub> N <sub>6</sub> O <sub>6</sub> S	Found 56.59 Calc. 56.67	2.86 2.67	14.66 14.37	6.75 6.57
9.	<i>p</i> -Nitrophenyl	202	70	Red	Deep red	C <sub>23</sub> H <sub>13</sub> N <sub>6</sub> O <sub>6</sub> S	Found 56.36 Calc. 56.67	2.91 2.67	14.76 14.37	6.88 6.57
10.	<i>s</i> -Tribromophenyl	228	80	Dark red	Deep red	C <sub>23</sub> H <sub>9</sub> Br <sub>3</sub> N <sub>3</sub> O <sub>2</sub> S	Found 31.94 Calc. 31.69	1.42 1.03	4.56 4.82	3.88 3.67

## NOTES

TABLE 2 : (2-Oxo-3-INDOLINYLDENE)-3-ARYL-2, 4-THIAZOLI DINEDIONES

Sl.No.	Ar. group	m.p. °C	Yield %	Colour	Colour in conc. H <sub>2</sub> SO <sub>4</sub>	Molecular Formula	Analysis %			
							C	H	N	S
1.	<i>p</i> -Fluorophenyl	217-18	72	Brown red	Dark red	C <sub>17</sub> H <sub>9</sub> FN <sub>2</sub> O <sub>3</sub> S	Found 60.28 Calc. 60.00	2.34 2.65	8.55 8.23	9.14 9.41
2.	<i>p</i> -Chlorophenyl	252	81	Brown red	Deep orange yellow	C <sub>17</sub> H <sub>9</sub> ClN <sub>2</sub> O <sub>3</sub> S	Found 57.58 Calc. 57.22	2.88 2.52	7.14 7.85	8.66 8.98
3.	<i>p</i> -Bromophenyl	Shrinks at 180 and slowly decomposes afterwards	78	Brown	Dark choco- late red	C <sub>17</sub> H <sub>9</sub> BrN <sub>2</sub> O <sub>3</sub> S	Found 50.56 Calc. 50.87	2.48 2.24	6.67 6.98	7.71 7.98
4.	<i>o</i> -Iodophenyl	269-70	90	Red	Pinkish red	C <sub>17</sub> H <sub>9</sub> IN <sub>2</sub> O <sub>3</sub> S	Found 45.26 Calc. 45.53	2.31 2.01	6.55 6.25	7.46 7.14
5.	<i>o</i> -Hydroxyphenyl	280-82	64	Dark red	Yellowish red	C <sub>17</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> S	Found 60.66 Calc. 60.35	2.59 2.96	8.56 8.28	9.81 9.47
6.	<i>m</i> -Hydroxyphenyl	290	65	Red	Deep red	C <sub>17</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> S	Found 60.72 Calc. 60.35	2.58 2.96	8.48 8.28	9.12 9.47
7.	<i>p</i> -Hydroxyphenyl	300	74	Red	Dark red	C <sub>17</sub> H <sub>10</sub> N <sub>2</sub> O <sub>4</sub> S	Found 60.82 Calc. 60.35	2.48 2.96	8.68 8.28	9.08 9.47
8.	<i>m</i> -Nitrophenyl	252	72	Red	Deep orange red	C <sub>17</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub> S	Found 55.34 Calc. 55.59	2.77 2.45	11.26 11.44	8.36 8.72
9.	<i>p</i> -Nitrophenyl	205-6	70	Yellowish red	Light brown	C <sub>17</sub> H <sub>9</sub> N <sub>3</sub> O <sub>3</sub> S	Found 55.91 Calc. 55.59	2.14 2.45	11.72 11.44	8.48 8.72
10.	2,4-Dichlorophenyl	Slowly decomposes above 160	74	Reddish Brown	Chocolate red	C <sub>17</sub> H <sub>8</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>3</sub> S	Found 52.48 Calc. 52.17	2.44 2.05	7.52 7.16	8.55 8.18

in excess of cold water. The precipitate thus obtained was filtered, washed several times with hot water followed by dilute acetic acid and finally with ethanol. The product was obtained as brown red crystals, m.p. : 217°-18°; yield 1.8 g (72%).

The thioindigoid dyes prepared by the above method are listed in Table 2.

## References

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Chemical Examination of *Clausena Excavata*

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Manuscript received 15 July 1973; accepted 22 August 1973

THE isolation and structure elucidation of some novel coumarins and carbazoles, viz., clausenin, clausenidin, heptazoline and heptaphylline from the root and stem bark of *Clausena heptaphylla*<sup>1-5</sup>, and dentatin, nor-dentatin along with imperatorin from the root-bark of *C. dentata*<sup>6</sup> were reported earlier.

In the present communication we report the isolation and characterization of two coumarins viz., clausenin and clausenidin from the root and stem bark of *C. excavata*. The petroleum ether (b.p. 60°-80°) extract of the root and stem bark of *C. excavata* on column chromatography over silica gel furnished a compound m.p. 135°-36°. Another compound m.p. 156°-57°, was isolated from the same extract by preparative t.l.c. over silica gel G.

The compound m.p. 135°-36°, C<sub>19</sub>H<sub>20</sub>O<sub>5</sub> (M<sup>+</sup> 328), was yellow in colour, and showed single spot in t.l.c. (solvent : benzene : chloroform = 1 : 1 v/v; chloroform : methanol = 95 : 5 v/v). It gave a positive ferric chloride test. Its UV and IR spectra indicated the compound to be a coumarin :  $\lambda_{max}^{EtOH}$  222, 284 and 328 nm;  $\nu_{max}^{Nujol}$  1740 cm<sup>-1</sup> (coumarin lactone ring) and 1650 cm<sup>-1</sup> (chelated carbonyl). The physical properties of the compound was found to be very similar to those reported for clausenidin. The identity of the two compounds was established by comparison of mixed m.p., t.l.c., UV and IR spectra. The compound m.p. 156°-57° had the formula C<sub>14</sub>H<sub>12</sub>O<sub>5</sub>, (M<sup>+</sup> 260), and showed a single spot in t.l.c. (solvent : same as for the previous compound). It gave positive ferric chloride test. Its m.p., UV ( $\lambda_{max}^{EtOH}$  216, 279 and 320 nm) and IR [ $\nu_{max}^{Nujol}$  1728 cm<sup>-1</sup> (coumarin lactone), 1639 cm<sup>-1</sup> (chelated carbonyl)] spectra were very similar to those reported for clausenin. The identity was established by comparison of mixed m.p., t.l.c., UV and IR spectra.