

## Structural studies in naturally occurring anthraquinones using melting points

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### ABSTRACT

When a OH group of an anthraquinone changes to OMe : an increase in mp is indicative of chelated OH methylation; a decrease of mp up to 40°C also depicts chelated OH methylation ; a decrease of mp by 50°C or more hints nonchelated OH methylation.

**Key words:** Anthraquinones, melting point, methylation.

### INTRODUCTION

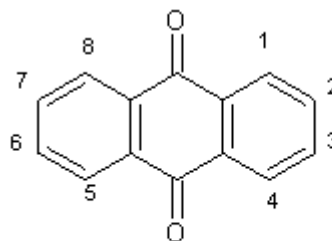
It has already been shown that <sup>1</sup>H NMR O-alkylation shifts are helpful in locating the site of O-methylation in naturally occurring anthraquinones. It has been observed further that a change in mp also helps in ascertaining the position of O-methylation. Typical trends for a change of mp have been observed for the first time for a OH methylation.

A comparison of mp of 1-hydroxy-3-methyl-anthraquinone (9, mp 178°C) and that of 1-methoxy-3-methylanthraquinone (10, mp 190-191°C) shows that there is increase of mp (10 : 9 has  $\Delta mp = (+)12-13^\circ C$ ). The (+) sign indicates that the mp is more in 10 than that in 9. That there is increase in mp on methylation of a chelated OH is also evident from other comparisons 14 : 13, 32 : 30 and 34 : 33 (Table 2) The mps of anthraquinones have been placed in Table 1, and change of mps have been shown in Table 2.

A decrease of mp has also been observed in O-methylation of a chelated OH and this decrease is numerically less than 40°C as evident from comparisons 2 : 1, 6 : 5, 12 : 11, 16 : 15, 18 : 17, 20 : 19, 27 : 26, 29 : 28 and 36 : 35 (Table 2).

When a nonchelated OH undergoes methylation, the decrease in mp is always numerically equal to or more than 45°C, and this becomes evident from several comparisons shown in Table 2.

Though  $\Delta mp$  is helpful in making a decision whether chelated or nonchelated OH has undergone methylation yet to be on safer side one may not draw a conclusion when the change in mp has the range - 40 to - 50°C.



1 - 38

Scheme 1: For substituents see table 1

Table 1: Melting points of anthraquinones

Substituents				Compd.	mp
OH	OMe	Me	CHO	No. <sup>reference</sup>	°C
1	-	-	-	1 <sup>2</sup>	194-195
-	1	-	-	2 <sup>2</sup>	169-170
2	-	-	-	3 <sup>3</sup>	306
-	2	-	-	4 <sup>3</sup>	195-196
1	-	2	-	5 <sup>3</sup>	185-186
-	1	2	-	6 <sup>3</sup>	154-156
3	-	2	-	7 <sup>2</sup>	302
-	3	2	-	8 <sup>2</sup>	195-196
1	-	3	-	9 <sup>4</sup>	178
-	1	3	-	10 <sup>4</sup>	190-191
1,2	-	3	-	11 <sup>5</sup>	250-251
2	1	3	-	12 <sup>5</sup>	220
1,3	-	-	-	13 <sup>6</sup>	269-270
3	1	-	-	14 <sup>6</sup>	311-313
1	3	-	-	15 <sup>6</sup>	193-194
-	1,3	-	-	16 <sup>6</sup>	154-155
1,3	-	2	-	17 <sup>5</sup>	302
3	1	2	-	18 <sup>5</sup>	291
1,3	-	-	2	19 <sup>7</sup>	220-221
3	1	-	2	20 <sup>7</sup>	212
1,2,3	-	-	-	21 <sup>8</sup>	312-313
1,3	2	-	-	22 <sup>8</sup>	218
1,2	3	-	-	23 <sup>6</sup>	242-243
3	1,2	-	-	24 <sup>8</sup>	238
2	1,3	-	-	25 <sup>9</sup>	212
1	2,3	-	-	26 <sup>6</sup>	166-168
-	1,2,3	-	-	27 <sup>9</sup>	164-166
1,3,5	-	-	-	28 <sup>10</sup>	249-251
3,5	1	-	2	29 <sup>10</sup>	248
1,6,8	-	3	-	30 <sup>11</sup>	255
1,8	6	3	-	31 <sup>11</sup>	207
1,6	8	3	-	32 <sup>12</sup>	301-303
1,4	-	2	-	33 <sup>13</sup>	175-176
1	4	2	-	34 <sup>14</sup>	188-190
1,5	-	2	-	35 <sup>15</sup>	196-197
1	5	2	-	36 <sup>15</sup>	189-191
4,7	1,5,6	2	-	37 <sup>16</sup>	213-215
4	1,5,6,7	2	-	38 <sup>16</sup>	168-169

**Table 2 : Change of melting points ( $\Delta$ mp, °C) on methylation**

Compounds	$\Delta$ mp	Compounds	$\Delta$ mp	Compounds	$\Delta$ mp
Methylation of chelated OH					
2 : 1 <sup>a</sup>	<sup>i</sup> (-) 25	6 : 5 <sup>a</sup>	(-) 30 - 31	10 : 9 <sup>a</sup>	<sup>i</sup> (+) 12 -13
12 : 11 <sup>a</sup>	(-) 30-31	14 : 13 <sup>a</sup>	(+) 32 -33	16 : 15 <sup>a</sup>	(-) 29
18 : 17 <sup>a</sup>	(-) 11	20 : 19 <sup>a</sup>	(-) 8 - 9	27 : 26 <sup>a</sup>	(-) 2
29 : 28 <sup>a</sup>	(-) 1-3	32 : 30 <sup>b</sup>	(+) 46 -48	34 : 33 <sup>c</sup>	(+) 13-14
36 : 35 <sup>d</sup>	(-) 37-38				
Methylation of nonchelated OH					
4 : 3 <sup>e</sup>	(-) 110-111	15 : 13 <sup>f</sup>	(-) 76	16 : 14 <sup>f</sup>	(-) 157-158
22 : 21 <sup>e</sup>	(-) 94-95	23 : 21 <sup>f</sup>	(-) 70	26 : 22 <sup>f</sup>	(-) 50-52
27 : 22 <sup>e</sup>	(-) 52-54	26 : 23 <sup>e</sup>	(-) 75 - 76	27 : 24 <sup>f</sup>	(-) 72-74
31 : 30 <sup>g</sup>	(-) 48	38 : 37 <sup>h</sup>	(-) 45 - 46		

<sup>a</sup>1-O-Methylation ; <sup>b</sup>8-O-Methylation ; <sup>c</sup>4-O-Methylation ; <sup>d</sup>5-O-Methylation ; <sup>e</sup>2-O-Methylation ; <sup>f</sup>3-O-Methylation ; <sup>g</sup>6-O-Methylation ; <sup>h</sup>7-O-Methylation ; <sup>i</sup>(-) sign shows that the mp of 2 is less than that of 1 ; <sup>i</sup>(+) sign shows that the mp of 10 is more than that of 9.

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