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The usefulness of 3-iodoindoles available for introduction of an indole unit is presented. The reaction of various halo-3-iodoindoles with 1,4-naphthoquinone gave the corresponding 2-(3-indolyl)-1,4-naphthoquinones in moderate yields. The 3-iodoindole was used for synthesis of a compound containing both naphthazarin and indole skeletons.

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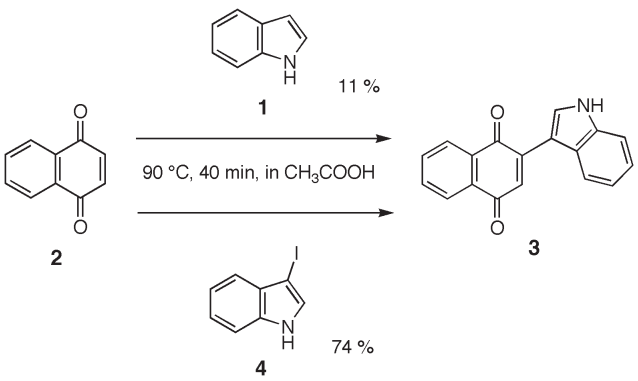
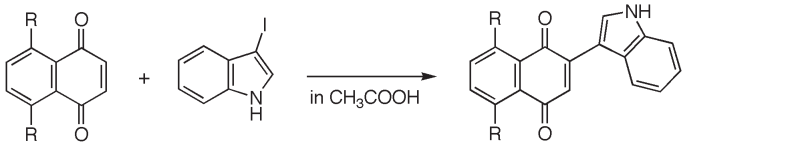
An indole unit occurs naturally in indole alkaloids and many of the naturally occurring compounds have physiologically important activity [1]. In previous papers [2,3] we have reported syntheses of Tyrian purple [4] and its related compounds using 3-iodoindoles. 3-Iodoindole compounds are labile, and so are not commercially available. However, the compounds are easily synthesized from the corresponding indoles.

Some reports have appeared concerning the reaction of indoles with 1,4-naphthoquinones. For example, Bu'Lock and Mason [5] reported that the reaction of indole (**1**) with 1,4-naphthoquinone (**2**) gave 2-(3-indolyl)-1,4-naphthoquinone (**3**) in acetic acid at room temperature for 7 days without describing the yield. Prota *et al*. [6] found that the reaction of **1** with **2** afforded **3** in acidic ethanol at room temperature for an hour in moderate yield. In the course of

Scheme 1



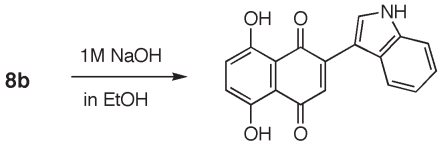
Scheme 2



7a: R=OMe
7b: R=OAc

4

8a: R=OMe (51%)
8b: R=OAc (40%, by-product: **8c**, 20%)

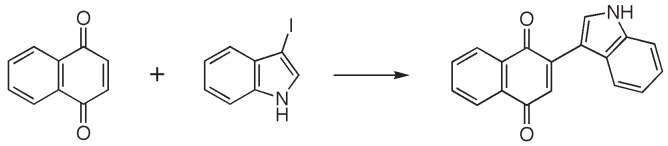


8b

9

Table 1

Reaction of 3-Iodoindole (**4**) with 1,4-Naphthoquinone (**2**) under Various Conditions



2 **4** **3**

Entry	Solvent	Temp	Time	Yield / % [a]
1	CH_3COOH	rt	3 h	44
2	CH_3COOH	rt	5 days	41
3	CH_3COOH	90°C	40 min	74
4	CH_3COOH	reflux	5 min	51
5	CH_3COOH	reflux	30 min	25
6	CH_3CN	reflux	1 h	58
7	$CHCl_3$	rt	3 h	34
8	C_2H_5OH	reflux	1 h	0

[a] Isolated yield.

our synthetic study of natural products containing an indole moiety, we have found that 3-iodoindole is a favorable reagent for introduction of the indole unit into **2**. The present paper describes syntheses of 2-(3-indolyl)-1,4-naphthoquinones and a compound having both naphthazarin and indole skeletons using 3-iodoindoles.

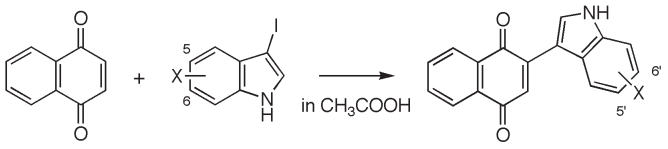
In our hands the reported procedure [5] gave **3** in only 16 % yield. Therefore, we have investigated a difference of reactivity in **1** and 3-iodoindole (**4**). The reaction of **4** with **2** in acetic acid at 90 °C for 40 minutes gave **3** in 74 % yield. On the other hand, treatment of **1** with **2** afforded **3** under the same reaction conditions in only 11 % yield (Scheme 1). The results seem to indicate that **4** is very favorable for introduction of an indole unit in comparison with **1**. The reactions of **4** with **2** are shown in Table 1 under various conditions. Further refluxing time decreased the yield in acetic acid because of decomposition of **4** (entry 5). Interestingly the product **3** was also obtained in moderate yield in case of acetonitrile as solvent (entry 6). On the basis of the results, the reaction of various halo-3-iodoindoles (**5**) with **2** was run (Table 2). Since compounds **5** were somewhat stable to heat relative to **4**, the reaction was kept under reflux in acetic acid.

The structural determination of **6e** is described as a typical example. The ^1H NMR spectrum shows the signals at δ 7.26 (singlet) and 8.22 (doublet) due to 3-H and 2'-H, respectively. The mass spectrum clearly exhibits the molecular ion peak at m/z 291. The data as well as the elemental analysis indicate the structure of **6e**.

Naturally occurring shikonin [7], which is a potent pharmaceutical substance with a wide spectrum of biological properties, contains a naphthazarin (5,8-dihydroxy-1,4-naphthoquinone) moiety. On the other hand, asterriquinones [8], which exhibit a range of biological activities, have both indole and benzoquinone moieties. Accordingly, we next have synthesized a compound **9**, which contains both moieties (Scheme 2).

Table 2

Reaction of Halo-3-iodoindoles (**5**) with 1,4-Naphthoquinone (**2**)



2 **5** **6**

Entry	Iodoindole	X	Temp	Time / min	Product	Yield / % [a]
1	**5a**	6-Br	reflux	70	**6a**	75
2	**5b**	5-Br	reflux	180	**6b**	69
3	**5c**	6-Cl	reflux	90	**6c**	73
4	**5d**	5-Cl	reflux	60	**6d**	64
5	**5e**	6-F	reflux	20	**6e**	61
6	**5f**	5-F	reflux	180	**6f**	56

[a] Isolated yield.

Treatment of **4** with 5,8-dimethoxy-1,4-naphthoquinone (**7a**) [9] gave 2-(3-indolyl)-5,8-dimethoxy-1,4-naphthoquinone (**8a**) in acetic acid at 90 °C for 20 minutes in 51 % yield. Attempts to do demethylation [10] of **8a** using $AlCl_3$, BBr_3 *etc.* were unsuccessful. Thus, the starting material **7a** was replaced by 5,8-diacetoxy-1,4-naphthoquinone (**7b**) [11]. The reaction of **4** with **7b** gave 5,8-diacetoxy-2-(3-indolyl)-1,4-naphthoquinone (**8b**) in

refluxing acetic acid for 5 minutes in 40 % yield with a by-product, 5/8-acetoxy-5/8-hydroxy-2-(3-indolyl)-1,4-naphthoquinone (**8c**). The structure of **8c** was mainly determined by its ^{1}H NMR spectrum, which shows the hydroxy (s, 1H) at δ 12.79 and the methyl protons (s, 3H) at δ 2.47. Hydrolysis of **8b** was carried out in aqueous ethanol including sodium hydroxide to give our desired product, 5,8-dihydroxy-2-(3-indolyl)-1,4-naphthoquinone (**9**) in 65 % yield. The structural assignment of **9** was based on its ^{1}H NMR spectrum, which shows the quinone (s, 1H) at δ 7.30, the amine (s, 1H) at δ 12.14, and the two hydroxy protons at δ 12.61 and 12.82.

In summary, we found that 3-iodoindoles are favorable reagents for introduction of an indole unit. Compound **9**, which contains both naphthazarin and indole skeletons was synthesized using this approach.

EXPERIMENTAL

^{1}H NMR and ^{13}C NMR spectra were taken on a JEOL JNM-EX90A (90 MHz) and JEOL JNM-A500 (500 MHz) spectrometers in chloroform-d and dimethyl sulfoxide-d_6 at room temperature. Chemical shifts are given in ppm relative to tetramethylsilane as an internal reference standard. EI mass spectra were perforrmed with a JEOL JMS-SX 102A mass spectrometer. Infrared spectra were recorded on a Shimadzu IR 470 spectophotormeter as potassium bromide pellets. Melting points were observed with a Yanaco MS-S3 micro melting point apparatus (hot-plate type). Elemental analyses were determined with a Yanaco CHN Corder MT-3. For preparative column chromatography, Wakogel C-200 silica gel was employed. Thin- layer chromatography (TLC) was accomplished on precoated plates of silica gel $60F_{254+365}$ (Merck). 5- and 6-Haloindoles were purchased from Tokyo Kasei Kogyo Co. Ltd (Tokyo, Japan).

General Procedure for Iodination of Indoles.

Iodination of 6-bromoindole is described as a typical example. To a solution of 6-bromoindole (100 mg, 0.51 mmol) in methanol (10 ml) was added sodium hydroxide (20 mg, 0.51 mmol). After the mixture was stirred at room temperature for 10 minutes, iodine (129 mg, 0.51 mmol) and an aqueous solution (1 ml) of potassium iodide (59 mg, 0.51 mmol) were added. The mixture was further stirred at room temperature for 3 h, and then water was added. The resulting precipitate was collected by filtration, washed with water, and dried *in vacuo* to obtain 6-bromo-3-iodoindole (**5a**, 134 mg), which was used for the following reaction without purification because of its lability.

General Procedure for Synthesis of 2-(3-Indolyl)-1,4-naphthoquinones.

Synthesis of 2-(6-bromo-3-indolyl)-1,4-naphthoquinone (**6a**) is described as a typical example. A solution of 1,4-naphthoquinone (66 mg, 0.42 mmol) and 6-bromo-3-iodoindole (134 mg, 0.42 mol) in acetic acid (10 ml) was refluxed for 70 minutes. After the mixture was concentrated under reduced pressure, the residue was chromatographed on silica gel with chloroform to give **6a** (110 mg, 75 %).

2-(3-Indolyl)-1,4-naphthoquinone (**3**).

This compound was obtained as blackish-purple needles (ethyl acetate), mp 206.5 –208 °C (lit [6], 175 °C); ir (KBr): NH 3245, CO 1667, 1630 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide–d_6): δ 7.02 –7.25 (m, 2H, 5'- and 6'-H), 7.26 (s, 1H, 3-H), 7.54 (dd, 1H, 7'-H, J=1.2, 7.0 Hz), 7.84 – 7.86 (m, 2H, 6- and 7-H), 7.88 (d, 1H, 4'-H, J=7.6 Hz), 8.00 (m, 1H, 5-H), 8.08 (m, 1H, 8-H), 8.25 (d, 1H, 2'-H, J=2.7 Hz), 12.04 ppm (s, 1H, NH); ^{13} C nmr (dimethyl sulfoxide– d_6): δ 107.33 (3'-C), 112.58 (7'-C), 119.97 (6'-C), 121.24 (5'-C), 125.12 (5'- and 8'-C), 126.48 (8-C), 127.64 (3-C), 131.64, 132.45 (9-C, 10-C), 132.51 (2'-C), 133.52, 133.99 (6- and 7-C), 136.70 (9'-C), 142.06 (2-C), 184.09 (C=O), 184.95 ppm(C=O); ms: m/z (relative intensity) 273 (M$^+$, 100 %), 245 (22), 217 (36), 189 (13), 104 (22).

Anal. Calcd for $C_{18}H_{11}NO_2$: C, 79.11; H, 4.06; N, 5.13. Found: C, 78.69; H, 4.52; N, 5.10.

2-(6-Bromo-3-indolyl)-1,4-naphthoquinone (**6a**).

This compound was obtained as blackish-purple needles (ethyl acetate), mp 276 - 278 °C; ir: NH 3160, CO 1666, 1628 cm^{-1}; ^{1}H nmr (dimetyl sulfoxide-d_6): δ 7.24 (s, 1H, 3-H), 7.33 (dd, 1H, 5'-H, J=1.8, 8.6 Hz), 7.71 (d, 1H, 7'-H, J=1.8 Hz), 7.83 (d, 1H, 4'-H, J=8.6 Hz), 7.86 - 8.00 (m, 2H, 6- and 7-H), 8.02 (m, 1H, 5-H), 8.10 (m, 1H, 8-H), 8.23 (d, 1H, 2'-H, J=3.1 Hz), 12.10 ppm (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide -d_6): δ 107.60, 115.06, 115.09, 121.87, 123.91, 124.27, 125.24, 126.58, 128.59, 131.64, 132.43, 133.00, 133.74, 134.14, 137.62, 141.72, 184.21 (C=O), 184.73 ppm (C=O); ms: m/z (relative intensity) 353 (M+2, 100 %), 351 (M$^+$, 98), 272 (12), 216 (21), 104 (29).

Anal. Calcd for $C_{18}H_{10}BrNO_2$: C, 61.39; H, 2.86; N, 3.98. Found: C, 61.32; H, 2.92; N, 3.88.

2-(5-Bromo-3-indolyl)-1,4-naphthoquinone (**6b**).

This compound was obtained as reddish-purple grains (ethyl acetate:hexane = 1:1), mp 237 - 238 °C; ir: NH 3240, CO 1667, 1629 cm^{-1}; ^{1}H nmr (chloroform-d): δ 7.34 (d, 1H, 7'-H, J=8.5 Hz), 7.37 (s, 1H, 3-H), 7.39 (dd, 1H, 6'-H, J=1.8, 8.5 Hz), 7.74 - 7.79 (m, 2H, 6- and 7-H), 8.10 (d, 1H, 4'-H, J=1.8 Hz), 8.14 (m, 1H, 5-H), 8.17 (m, 1H, 8-H), 8.22 (d, 1H, 2'-H, J=3.1 Hz), 8.76 ppm (s, 1H, NH); ^{13}C nmr (chloroform-d): δ 108.65, 113.22, 115.35, 122.98, 125.90, 126.34, 126.94, 127.23, 130.21, 131.54, 132.16, 132.74, 133.45, 133.87, 134.90, 141.51, 185.17 (C=O), 185.22 ppm (C=O); ms: m/z (relative intensity) 353 (M+2, 91.8 %), 351 (M$^+$, 91.4 %), 274 (78), 273 (100), 272 (97), 245 (47), 244 (42), 217 (86), 216 (75), 189 (79).

Anal. Calcd for $C_{18}H_{10}BrNO_2$: C, 61.39; H, 2.86; N, 3.98. Found: C, 61.59; H, 3.18; N, 3.82.

2-(6-Chloro-3-indolyl)-1,4-naphthoquinone (**6c**).

This compound was obtained as blackish-purple needles (ethyl acetate), mp 272 -274 °C; ir: NH 3170, CO 1666, 1628 cm^{-1}; ^{1}H nmr (dimethyl sulfoxide-d_6): δ 7.21 (dd, 1H, 5'-H, J=1.8, 8.6 Hz), 7.25 (s, 1H, 3-H), 7.57 (d, 1H, 7'-H, J=1.8 Hz), 7.86 - 7.90 (m, 3H, 4'-, 6-, and 7-H), 8.02 (m, 1H, 5-H), 8.10 (m, 1H, 8-H), 8.25 (d, 1H, 2'-H, J=2.4 Hz), 12.10 ppm (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 107.58, 112.16, 121.33, 121.51, 124.00, 125.24, 126.58, 127.07, 128.55, 131.65, 132.43, 133.10, 133.74, 134.14, 137.19, 141.74, 184.22 (C=O), 184.74 ppm (C=O); ms: m/z (relative intensity) 309 (M+2, 35 %), 307 (M$^+$, 100), 279 (28), 216 (40), 175 (28), 113 (29), 104 (83).

Anal. Calcd for $C_{18}H_{10}ClNO_2$: C, 70.25; H, 3.28; N, 4.55. Found: C, 70.33; H, 3.35; N, 4.47.

2-(5-Chloro-3-indolyl)-1,4-naphthoquinone (**6d**).

This compound was obtained as blackish-purple needles (ethyl acetate), mp 221 - 222 °C; ir: NH 3230, CO 1659, 1630 cm^{-1}; ^1H nmr (dimeththyl sulfoxide - d_6): δ 7.21 (s, 1H, 3-H), 7.24 (dd, 1H, 6'-H, J=1.8, 8.6 Hz), 7.54 (d, 1H, 7'-H, J=8.6 Hz), 7.84 (d, 1H, 4'-H, J=1.8 Hz), 7.86 - 7.90 (m, 2H, 6- and 7-H), 8.02 (m, 1H, 5-H), 8.10 (m, 1H, 8-H), 8.23 (d, 1H, 2'-H, J=2.7 Hz), 12.16 (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide - d_6): δ 107.35, 114.02, 119.35, 122.48, 125.24, 125.75, 126.38, 126.38, 126.57, 128.78, 131.65, 132.38, 133.28, 133.72, 134.13, 135.20, 141.74, 184.22 (C=O), 184.67 ppm (C=O); ms: m/z (relative intensity) 309 (M+2, 36 %), 307 (M^+, 100), 221 (25), 216 (14), 147 (12), 104 (20).

Anal. Calcd for $C_{18}H_{10}ClNO_2$: C, 70.25; H, 3.28; N, 4.55. Found: C, 70.01; H, 3.50; N, 4.90.

2-(6-Fluoro-3-indolyl)-1,4-naphthoquinone (**6e**).

This compound was obtained as blackish-purple needles (ethyl acetate:hexane = 2:1), mp 254 - 256 °C; ir: NH 3165, CO 1665, 1620 cm^{-1}; ^1H nmr (dimethyl sulfoxide - d_6): δ 7.04 - 7.08 (m, 1H, 5'-H), 7.26 (s, 1H, 3-H), 7.31 (dd, 1H, 7'-H, J=2.4, 9.5 Hz), 7.86 - 7.90 (m, 3H, 4'-, 6-, and 7-H), 8.02 (m, 1H, 5-H), 8.10 (m, 1H, 8-H), 8.22 (d, 1H, 2'-H, J=2.4 Hz), 12.05 ppm (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 98.69 (d, 7'-C, J=25.9 Hz), 107.57 (3'-C), 109.41 (d, 5'-C, J=23.8 Hz), 121.34 (d, 4'-C, J=10.3 Hz), 121.93, 125.23, 126.58, 128.20, 131.66, 132.47, 132.88, 133.72, 134.13, 136.85 (d, 8'-C, J=12.4 Hz), 141.85, 159.08 (d, 6'-C, J=237 Hz), 184.22 (C=O), 184.81 ppm (C=O); ms, m/z (relative intensity) 291 (M^+, 100 %), 263 (56), 235 (79), 207 (23), 104 (67).

Anal. Calcd for $C_{18}H_{10}FNO_2$: C, 74.22; H, 3.46; N, 4.81. Found: C, 74.33; H, 3.56; N, 4.57.

2-(5-Fluoro-3-indolyl)-1,4-naphthoquinone (**6f**).

This compound was obtained as blackish-purple needles (ethyl acetate:hexane = 5:1), mp 223 - 225 °C; ir: NH 3370, CO 1658, 1640 cm^{-1}; ^1H nmr (chloroform-d): δ 6.99 - 7.03 (m, 1H, 6'-H), 7.31 (s, 1H, 3-H), 7.35 (dd, 1H, 7'-H, J=4.6, 8.9 Hz), 7.60 (dd, 1H, 4'-H, J=2.1, 10.1 Hz), 7.73 -7.75 (m, 2H, 6- and 7-H), 8.12 (m, 1H, 5-H), 8.14 (m, 1H, 8-H), 8.22 (s, 1H, 2'-H), 9.60 ppm (s, 1H, NH); ^{13}C nmr (chloroform-d): δ 105.9 (d, 4'-C, J=24.8 Hz), 111.5 (d, 6'-C, J=26.9 Hz), 112.7 (d, 9'-C, J=10.3 Hz), 112.8 (d, 7'-C, J=10.4 Hz), 125.8, 126.9, 129.3, 132.2, 132.6, 132.7, 132.8, 133.0, 133.4, 133.8, 142.0, 159.1 (d, 5'-C, J=238 Hz), 185.3 (C=O), 185.5 (C=O); ms: m/z (relative intensity) 291 (M^+, 100 %), 263 (54), 235 (72), 207 (20), 104 (49).

Anal. Calcd for $C_{18}H_{10}FNO_2$: C, 74.22; H, 3.46; N, 4.81. Found: C, 74.01; H, 3.54; N, 4.79.

2-(3-Indolyl)-5,8-dimethoxy-1,4-naphthoquinone (**8a**).

This compound was obtained as reddish-orange needles (chloroform:ethanol = 10:1), mp 285–287 °C; ir: NH 3325, CO 1641 cm^{-1}; ^1H nmr (dimethyl sulfoxide - d_6): δ 3.87 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 7.02 (s, 1H, 3-H), 7.17 -7.23 (m, 2H, 5'- and 6'-H), 7.50 - 7.52 (m, 3H, 6-, 7-, and 7'-H), 7.80 (d, 1H, 4'-H, J=7.3 Hz), 8.12 (d, 1H, 2'-H, J=2.8 Hz), 11.90 ppm (s, 1H, NH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 56.56 (CH_3), 56.67 (CH_3), 106.88, 112.41, 119.85, 120.35, 120.49, 120.85, 120.91, 122.07, 122.25, 125.12, 127.58, 131.41, 136.62, 142.27, 152.33, 152.81, 183.40 (C=O), 184.81 ppm (C=O); ms: m/z (relative intensity) 333 (M^+, 100 %), 316 (23), 304 (42), 290 (22), 163 (28), 141 (23), 130 (36), 117 (38).

Anal. Calcd for $C_{20}H_{15}NO_4$: C, 72.06; H, 4.54; N, 4.20. Found: C, 71.78; H, 4.51; N, 4.04.

5,8-Diacetoxy-2-(3-indolyl)-1,4-naphthoquinone (**8b**).

This compound was obtained as blackish-purple grains (ethyl acetate:hexane = 5:1), mp 235 - 237 °C; ir: NH 3375, CO 1760, 1665, 1633 cm^{-1}; ^1H nmr (chloroform-d): δ 7.19 (s, 1H, 3-H), 7.22 - 7.27 (m, 2H, 5'- and 6'-H), 7.35 (d, 1H, 6/7-H, J=8.9 Hz), 7.39 (d, 1H, 6/7-H, J=8.9 Hz), 7.40 (dd, 1H, 7'-H, J=1.8, 7.0 Hz), 7.83 (dd, 1H, 4'-H, J=1.8, 8.9 Hz), 8.06 (d, 1H, 2'-H, J=2.7 Hz), 8.73 ppm (s, 1H, NH); ^{13} C nmr (chloroform-d): δ 21.19 ($2CH_3$), 108.39, 111.91,120.30,121.90, 123.38, 124.55, 125.39, 125.60, 129.50, 130.19, 130.49, 130.94, 136.27, 142.11, 146.99, 147.58, 169.51 (CH_3CO), 169.66 (CH_3CO), 183.21 (C=O), 183.88 ppm (C=O); ms: m/z (relative intensity) 389 (M^+, 31 %), 347 (37), 305 (100), 276 (17), 141 (16).

Anal. Calcd for $C_{22}H_{15}NO_6$: C, 67.87; H, 3.88; N, 3.60. Found: C, 67.63; H, 4.00; N, 3.51.

5/8-Acetoxy-5/8-hydroxy-2-(3-indolyl)-1,4-naphthoquinone (**8c**).

This compound was obtained as blackish-purple needles (ethyl acetate:hexane = 5:1), mp 177 - 179 °C; ir: NH 3355, CO 1756, 1616 cm^{-1}; ^1H nmr (chloroform-d): δ 2.47 (s, 3H, CH_3), 7.25 - 7.31 (m, 5H, 3-, 5'-, 6'-, 6-, and 7-H), 7.38 (m, 1H, 7'-H), 7.90 (m, 1H, 4'-H), 8.13 (d, 1H, 2'-H, J=3.1 Hz), 8.77 (broad, 1H, NH), 12.79 ppm (s, 1H, OH); ^{13}C nmr (chloroform-d): δ 21.21 (CH_3), 108.92, 112.00, 114.84, 120.40, 122.14, 122.85, 123.57, 125.42, 125.70, 127.83, 131.85, 132.11, 136.24, 142.74, 143.81, 159.52 (C-OH), 169.89 ($COCH_3$), 183.64 (C=O), 189.75 ppm (C=O); ms: m/z (relative intensity) 347 (M^+, 44 %), 306 (62), 305 (100), 277 (21), 276 (21), 220 (15).

Anal. Calcd for $C_{20}H_{13}NO_5$: C, 69.16; H, 3.77; N, 4.03. Found: C, 68.87; H, 3.88; N, 3.96.

Hydrolysis of 5,8-Diacetoxy-2-(3-indolyl)-1,4-naphthoquinone (**8b**).

To a solution of **8b** (31 mg, 7.96×10^{-2} mmol) in ethanol (5 ml) was added aqueous 1 *M* sodium hydroxide (10 ml). After the mixture was stirred at room temperature for 2 h, acetic acid (1.5 ml) and water (10 ml) were added. The resulting precipitate was collected by filtration, washed with water, and dried. The crude product was purified by thin - layer chromatography on silica gel to give **9** (15.8 mg, 65 %). Recrystallization from acetonitrile gave blackish-purple needles, mp 246 - 248 °C; ir: NH 3180, CO 1591 cm^{-1}; ^1H nmr (dimethyl sulfoxide-d_6): δ 7.22 -7.27 (m, 2H, 5'- and 6'-H), 7.30 (s, 1H, 3-H), 7.36 (d, 1H, 6/7-H, J=9.5 Hz), 7.40 (d, 1H, 6/7-H, J=9.5 Hz), 7.55 (dd, 1H, 7'-H, J=1.4, 6.6 Hz), 7.90 (dd, 1H, 4'-H, J=1.3, 7.0 Hz), 8.33 (d, 1H, 2'-H, J=3.1 Hz), 12.14 (s, 1H, NH), 12.61 (s, 1H, OH), 12.82 ppm (s, 1H, OH); ^{13}C nmr (dimethyl sulfoxide-d_6): δ 107.22, 111.43, 112.60, 112.70, 120.04, 121.52, 122.78, 125.05, 127.43, 129.06, 130.01, 133.07, 136.69, 142.98, 157.23 (C-OH), 158.51 (C-OH), 185.97 (C=O), 186.67 ppm (C=O); ms: m/z (relative intensity) 305 (M^+, 100 %), 277 (18), 260 (11), 220 (13), 153 (14), 141 (16), 108 (19).

Anal. Calcd for $C_{18}H_{11}NO_4$: C, 70.82; H, 3.63; N, 4.59. Found: C, 71.10; H, 4.16; N, 4.60.

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