# An Expeditious Synthesis of Javanicin

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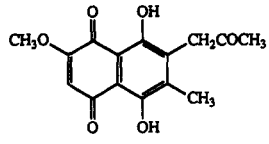
The fungal metabolite javanicin (1) was isolated nearly 50 years ago[1] and its constitution definitely established by synthesis some two decades later.[2,3] Although interest in its antibiotic properties has receded, the substance, as a trisubstituted naphthazarin, still presents a compelling preparative challenge since a direct method for the regiospecific elaboration of such compounds remains elusive and structures of many analogous naturally occurring pigments like lomazarin, haemoventosin, erythrostominone, etc. have not as yet been confirmed by synthesis.[1]



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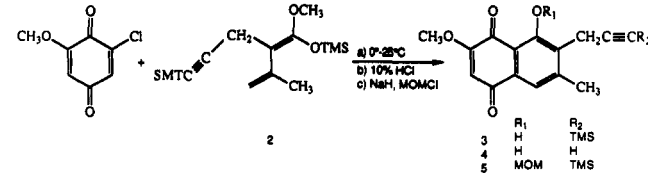
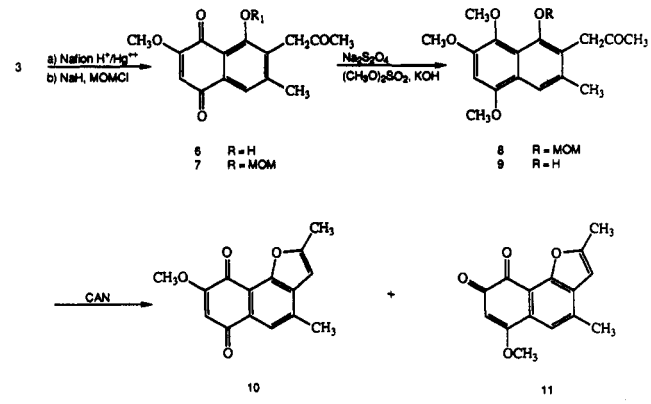
One of the most convenient means of obtaining a particular isomer of an unsymmetrically substituted naphthazarin entails only the oxidation of the corresponding partially protected polyhydroxynaphthalene.[4] Ready access to an appropriately substituted naphthol such as 4, incorporating the complete carbon skeleton of the end product, is moreover accessible by the regiospecific cycloaddition methodology for which the required diene follows directly from a selective $\alpha$-propargylation of a 3-methoxycrotonate[5] (Scheme I). In principle the oxidative step can then proceed either with or without prior hydration of the triple bond.

In the first instance, the original strategy consisting in the desilylation of quinone 3 and hydration of alcyne 4 was improved by carrying out the two steps simultaneously in the presence of mercury-impregnated Nafion-H.[6] Conversion of juglone 6 to MOM either 7[7] followed by reductive methylation[8,9] of the quinone and cleavage of the protective group afforded naphthol 9.[10] Finally, oxidation of the latter with CAN,[4h] a method used effectively in the preparation of some ventiloquinones,[11] provided only a 1:3 mixture of the corresponding *o*- and *p*-anhydroquinones 11[12] and 10[13] (Scheme II).

**Scheme I**



**Scheme II**



A more successful route was explored by first converting propargyljuglone 3 to trimethoxynaphthol 13 in an overall yield of 81% for the three steps. Thus, after initial protection of the hydroxyquinone as the MOM ether (i.e., 5), reductive methylation was also found to occur with fortuitous desilylation. Cleavage of MOM ether 12 could then be conducted under mild conditions and in high yield (94%) using a catalytic amount of acid in methanol[14] to provide 13. The oxidation step carried out with an iodonium compound that had given excellent results in the case of some ventiloquinones[11] provided only a disappointing 43% of the expected naphthazarin trimethyl ether 14. However, upon turning to a less promising reagent, CAN provided the desired quinone 14 in very good yield (80%). The latter was accompanied by 10% of the corresponding naphthazarin but surprisingly the yield of this peri-bisdemethylated product could not be increased with the use of an excess of the oxidizing agent.

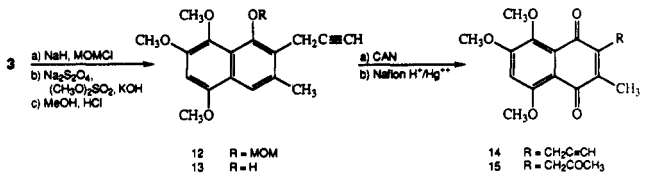
The next to last step of the synthesis involving the hydration of the triple bond was examined under various conditions all of which implicated the effective Hg/Nafion-H complex. When conducted in methanol at reflux temperature, the reaction provided a 60% yield of a 7:3

(1) Thomson, R. H. *Naturally Occurring Quinones*, 2nd ed.; Academic Press: London, 1971.
(2) Hardegger, E.; Widmer, E.; Steiner, K.; Pfiffner, A. *Helv. Chim. Acta* **1964**, *47*, 2031.
(3) Widmer, E.; Meyer, J. W.; Walser, A.; Hardegger, E. *Helv. Chim. Acta* **1965**, *48*, 538.
(4) (a) Hardegger, E.; Steiner, K.; Widmer, E.; Schmidt. T. H. *Helv. Chim. Acta* **1964**, *47*, 2017. (b) Barton, D. H. R.; Cottier, L.; Freund, K.; Luini, F.; Magnus, P. D.; Salazar, I. *J. Chem. Soc., Perkin Trans. 1* **1976**, 499. (c) Katagiri, N.; Nakano, J.; Kato, T. *J. Chem. Soc., Perkin Trans. 1*, **1981**, 2710. (d) Krishna Kumari, L.; Pardhasaradhi, M. *Ind. J. Chem.* **1982**, *21B*, 1067. (e) Kjaer, D.; Kjaer, A.; Risbjerg, E. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2815. (f) Sibi, M. P.; Dankwardt, J. W.; Snieckus, V. *J. Org. Chem.* **1986**, *51*, 271. (g) Watanabe, M.; Hisamatsu, S.; Hotokezaka, H.; Furukawa, S. *Chem. Pharm. Bull. Jpn.* **1986**, *34*, 2810. (h) Laatsch, H. *Liebigs Ann. Chem.* **1986**, 1655; **1987**, 297. (i) Clive, D. L. J.; Khodabocus, A.; Vernon, P. G.; Angoh, A. G.; Bordeleau, L.; Middleton, D. S.; Lowe, C.; Killner, D. *J. Chem. Soc., Perkin Trans. 1* **1991**, 1443.
(5) Caron, B.; Brassard, P. *Tetrahedron* **1991**, *47*, 4287; *Ibid*, in press.
(6) Olah, G. A.; Meidar, D. *Synthesis* **1978**, 671.
(7) Kluge, A. F.; Untch, K. G.; Fried, J. H. *J. Am. Chem. Soc.* **1972**, *94*, 7827.
(8) Kraus, G. A.; Man, T. O. *Synth. Commun.* **1986**, *16*, 1037.

(9) Compound 8: $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 2.17 (3 H, s, 6-$CH_2COCH_3$), 2.32 (3 H, s, 7-$CH_3$), 3.51 (3 H, s, 5-$OCH_2OCH_3$), 3.76, 3.96 and 3.97 (3 × 3 H, 3s, 1,3,4-$OCH_3$), 4.06 (2 H, s, 6-$CH_2COCH_3$), 5.04 (2 H, s, 5-$OCH_2OCH_3$), 6.63 (1 H, s, 2-H), and 7.82 (1 H, s, 8-H).
(10) Compound 9: $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 2.55 (3 H, s, 6-$CH_2COCH_3$), 2.59 (3 H, s, 7-$CH_3$), 3.98 (9 H, s, 1,3,4-$OCH_3$), 4.02 (2 H, s, 6-$CH_2COCH_3$), 6.50 (1 H, s, 2-H), 6.60 (1 H, s, 5-OH), and 7.73 (1 H, s, 8-H).
(11) Bergeron, D.; Brassard, P. *Heterocycles* **1992**, *34*, 1835.
(12) 2,4-Dimethyl-6-methoxy-8,9-dihydronaphtho[1,2-*b*]furan-8,9-dione (11): $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 2.53 (3 H, s, 4-$CH_3$), 2.56 (3 H, d, $J$ = 1.3 Hz, 2-$CH_3$), 3.99 (3 H, s, 6-$OCH_3$), 5.87 (1 H, s, 7-H), 6.43 (1 H, d, $J$ = 1.3 Hz, 3-H), and 7.50 (1 H, s, 5-H).
(13) 2,4-Dimethyl-8-methoxy-6,9-dihydronaphtho[1,2-*b*]furan-6,9-dione (10): $^1$H-NMR (200 MHz, $CDCl_3$) $\delta$ 2.54 (3 H, d, $J$ = 1.3 Hz, 2-$CH_3$), 2.58 (3 H, s, 4-$CH_3$), 3.88 (3 H, s, 8-$OCH_3$), 6.07 (1 H, s 7-H), 6.47 (1 H, d, $J$ = 1.3 Hz, 3-H), and 7.73 (1 H, s, 5-H).
(14) Auerbach, J.; Weinreb, S. M. *J. Chem. Soc., Chem. Commun.* **1974**, 298.

0022-3263/93/1958-0509$04.00/0 

**Scheme III**




mixture of the desired acetoxyl quinone 15 and the corresponding enol methyl ether. In boiling acetonitrile, the efficiency of the process was even lower, resulting in much decomposition, but when carried out at room temperature the process gave an 85% yield of quinone 15. Demethylation is known to proceed poorly in the presence of anhydrous $AlCl_3$ in dichloromethane[2] in the case of javanicin dimethyl ether and too extensively with other analogous compounds.[11] On the other hand, LiI in *tert*-butyl methyl ketone has been found to play a far more discriminating role.[11] Even so, at reflux temperature the product consisted of a 2:1 mixture of javanicin (1) and the corresponding 3-hydroxylated compound. However, after only 0.5 h at room temperature, javanicin could be obtained very selectively and with a high degree of conversion (85%) (Scheme III).

## Experimental Section

All melting points were taken for samples in capillary tubes and are not corrected. The NMR spectra were recorded at 200 and 50.3 MHz, respectively, in $CDCl_3$ using tetramethylsilane as internal standard. Merck silica gel $60F_{254}$ for dry column chromatography and ICN SiliTech 32-63 60A for flash chromatography were used throughout in a product-to-adsorbent ratio of 1:50–100. Elemental analyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

**1-Methoxy-3-methyl-1-(trimethylsiloxy)-2-(3-(trimethylsilyl)propargyl)-1,3-butadiene (2).** To a solution of LDA (0.066 mol) in THF (40 mL) at −78 °C was added (20 min), under $N_2$, methyl 3-methyl-2-propargyl-3-butenoate[5] (4.57 g; 30.0 mmol) in the same solvent (15 mL). After 30 min, the medium was warmed to 0 °C for 45 min and again cooled to −78 °C when chlorotrimethylsilane (11.4 mL; 90.0 mmol) in THF (12 mL) was added (45 min) and stirring continued for an additional hour. The reaction mixture was then allowed to come to rt, concentrated under vacuum, diluted with petroleum ether (bp 35–60 °C), and filtered (this procedure was repeated until salts no longer separated). The residue consisted of fairly pure but labile diene 2 as a single isomer (8.54 g; 96%): $^1$H-NMR δ 0.10 (9 H, s, 3′-TMS), 0.28 (9 H, s, 1-OTMS), 1.94 (3 H, dd, $J$ = 1.5, 0.8 Hz, 3-$CH_3$), 3.02 (2 H, s, 1′-H), 3.53 (3 H, s, 1-$OCH_3$), 4.88 (1 H, dq, $J$ = 2.0, 1.5 Hz, 4-H), and 4.95 (1 H, dq, $J$ = 2.0, 0.8 Hz, 4-H).

**5-Hydroxy-3-methoxy-7-methyl-6-(3-(trimethylsilyl)propargyl)-1,4-naphthoquinone (3).** A solution at 0 °C from diene 2 (0.50 mL; ~1.5 mmol) in dry THF (1 mL) and 2-chloro-6-methoxybenzoquinone[15] (0.345 g; 2.00 mmol) in the same solvent (8 mL) was stirred at the same temperature (2 h) then at 25 °C (2 h) and again cooled to 0 °C. A second portion of diene (0.5 mL) in THF (1 mL) was added, and stirring was continued at 0 °C (1 h) then at 25 °C (2 h). The reaction mixture at 0 °C was diluted with 10% aqueous HCl, stirred at the same temperature (30 min) and then at 25 °C (3 h), poured into water, and extracted with $CH_2Cl_2$ (2 × 200 mL). Purification by flash chromatography ($CH_2Cl_2$–$CCl_4$ (2:1) and then $CH_2Cl_2$) afforded naphthoquinone 3 (0.314 g; 48%): mp 173.0–173.5 °C (hexanes); IR $\nu_{max}$ (KBr) 2170, 1640, 1605 cm$^{-1}$; $^1$H-NMR δ 0.07 (9 H, s, 3′-TMS), 2.46 (3 H, s, 7-$CH_3$), 3.61 (2 H, s, 1′-H), 3.85 (3 H, s, 3-$OCH_3$), 6.02 (1 H, s, 2-H), 7.36 (1 H, s, 8-H), and 12.12 (1 H, s, 5-OH); $^{13}$C-NMR δ −0.03, 16.40, 20.55, 56.55, 84.89, 84.89, 101.90, 110.12, 112.24, 121.06, 129.89, 130.17, 147.95, 159.59, 160.19, 184.08, and 184.51; MS $m/z$ 328 (16) (M)$^+$, 69 (100). Anal. Calcd for $C_{18}H_{20}O_4Si$: C, 65.83; H, 6.14; Si, 8.55. Found: C, 65.85; H, 6.42, Si, 8.78.

**5-Hydroxy-3-methoxy-7-methyl-6-propargyl-1,4-naphthoquinone (4).** To a solution of quinone 3 (0.164 g; 0.500 mmol) in dry THF (10 mL) at 0 °C was added slowly (5 min) tetra-*n*-butylammonium fluoride (1.10 mL of a 1.00 M solution in THF; 1.10 mmol). The mixture was stirred at the same temperature (15 min) and then at 25 °C (2 h), poured into 10% aqueous HCl (200 mL), and extracted with $CH_2Cl_2$ (2 × 200 mL). Purification of the crude product by flash chromatography ($CHCl_3$) gave naphthoquinone 4 (0.121 g; 94%): mp 191.5–193.0 °C ($C_6H_6$–petroleum ether, bp 90–120 °C); IR $\nu_{max}$ (KBr) 2100, 1645, 1600 cm$^{-1}$; $^1$H-NMR δ 1.97 (1 H, t, $J$ = 2.7 Hz, 3′-H), 2.52 (3 H, s, 7-$CH_3$), 3.64 (2 H, d, $J$ = 2.7 Hz, 1′-H), 3.90 (3 H, s, 3-$OCH_3$), 6.10 (1 H, s, 2-H), 7.47 (1 H, s, 8-H), and 12.23 (1 H, s, 5-OH); MS $m/z$ 256 (100) (M)$^+$.

**5-Hydroxy-3-methoxy-7-methyl-6-(2-oxopropyl)-1,4-naphthoquinone (6).** A mixture of naphthoquinone 3 (0.263 g; 0.800 mmol), Nafion $H^+/Hg^{++}$ beads (~400 mg), water (1.3 mL), and methanol (14 mL) was heated to reflux for 7 h, filtered, poured into 10% aqueous HCl (200 mL), and extracted with $CH_2Cl_2$ (2 × 200 mL). The beads were washed with methanol and ether; the residue from all organic extracts was purified by flash chromatography on deactivated silica gel ($CH_2Cl_2$–AcOEt (10:1)) and gave quinone 4 (0.133 g; 61%): mp 216–217 °C ($C_6H_6$–petroleum ether, bp 90–120 °C); IR $\nu_{max}$ (KBr) 1700, 1645, 1600 cm$^{-1}$; $^1$H-NMR δ 2.28 and 2.35 (2 × 3 H, 2s, 3′,7-$CH_3$), 3.89 (2 H, s, 1′-H), 3.90 (3 H, s, 3-$OCH_3$), 6.11 (1 H, s, 2-H), 7.48 (1 H, s, 8-H), and 12.15 (1 H, s, 5-OH); $^{13}$C-NMR δ 20.72, 29.85, 40.85, 56.54, 110.22, 112.11, 120.86, 128.78, 130.06, 147.97, 160.07, 160.07, 183.99, 184.57, and 204.46; MS $m/z$ 274 (15) (M)$^+$, 232 (100). Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.39; H, 5.21.

**3-Methoxy-5-(methoxymethoxy)-7-methyl-6-(3-(trimethylsilyl)propargyl)-1,4-naphthoquinone (5).** A mixture of the sodium salt [obtained from naphthoquinone 3 (656 mg; 2.00 mmol) and 97% NaH (110 mg; 4.40 mmol) in THF (180 mL) at 50 °C (2 h) under $N_2$] and methoxymethyl chloride (0.63 g; 7.5 mmol) was heated to reflux (2 h), cooled, poured into 1% aqueous $Na_2CO_3$, and extracted with $CHCl_3$ (3 × 100 mL). The crude methoxymethyl ether (5) was used directly in the next step: $^1$H-NMR δ 0.09 (9 H, s, 3′-TMS), 2.55 (3 H, s, 7-$CH_3$), 3.65 (3 H, s, 5-$OCH_2OCH_3$), 3.76 (2 H, s, 1′-H), 3.87 (3 H, s, 3-$OCH_3$), 5.12 (2 H, s, 5-$OCH_2OCH_3$), 6.08 (1 H, s, 2-H), and 7.76 (1 H, s, 8-H); MS $m/z$ 372 (0.1) (M)$^+$, 73 (100).

**1,3,4-Trimethoxy-5-(methoxymethoxy)-7-methyl-6-propargylnaphthalene (12).** A solution of the methoxymethyl ether 5 obtained in the preceding paragraph, cetyltrimethylammonium bromide (120 mg; 0.320 mmol), $Na_2S_2O_4$ (2.20 g; 12.0 mmol), THF (40 mL), and $H_2O$ (16 mL) was shaken under $N_2$ until the color disappeared (~1 h). To this was added KOH (2.8 g; 50 mmol) in $H_2O$ (8 mL) and, after 15 min, dimethyl sulfate (3.0 g; 28 mmol). The mixture was stirred at rt for 14 h, poured into $H_2O$ (100 mL), and extracted with $CHCl_3$ (3 × 100 mL). Purification of the crude product by chromatography (dry column) (AcOEt–petroleum ether (1:4) bp 35–60 °C) afforded naphthalene 12 (568 mg; 86%): mp 131.5–132.5 °C (petroleum ether, bp 60–80 °C); IR $\nu_{max}$ (KBr) 3250, 2100, 1600, 1485 cm$^{-1}$; $^1$H-NMR δ 1.99 (1 H, t, $J$ = 2.6 Hz, 3′-H), 2.56 (3 H, s, 7-$CH_3$), 3.64 (3 H, s, 5-$OCH_2OCH_3$), 3.85 (2 H, d, $J$ = 2.6 Hz, 1′-H), 3.79, 3.97, and 3.98 (3 × 3 H, 3s, 1,3,4-$OCH_3$), 5.11 (2 H, s, 5-$OCH_2$-$OCH_3$), 6.63 (1 H, s, 2-H), and 7.82 (1 H, s, 8-H); $^{13}$C-NMR δ 16.88, 20.03, 55.80, 57.14, 57.76, 61.74, 68.12, 82.46, 95.12, 101.69, 118.98, 121.84, 122.39, 128.54, 132.94, 136.11, 148.91, 149.18, and 152.07; MS $m/z$ 330 (97) (M)$^+$, 255 (100).

**5-Hydroxy-1,3,4-trimethoxy-7-methyl-6-propargylnaphthalene (13).** A solution of methoxymethyl ether 12 (330 mg; 1.00 mmol) in methanol (100 mL) containing concd HCl (2 drops) was heated to reflux (45 min), cooled, poured into $H_2O$ (100 mL), and extracted with $CHCl_3$ (3 × 100 mL). Evaporation of the washed and dried extracts gave naphthol 13 (269 mg; 94%): mp 128.0–129.0 °C (methanol); IR $\nu_{max}$ (KBr) 3320, 3270, 2105 cm$^{-1}$; $^1$H-NMR δ 1.97 (1 H, t, $J$ = 2.7 Hz, 3′-H), 2.52 (3 H, s, 7-$CH_3$), 3.71 (2 H, d, $J$ = 2.7 Hz, 1′-H), 3.94, 3.95, and 4.01 (3 × 3 H, 3s, 1,3,4-$OCH_3$), 6.54 (1 H, s, 2-H), 7.48 (1 H, s, 8-H), and 10.07 (1

(15) Raiford, L. C.; Lichty, J. G. *J. Am. Chem. Soc.* **1930**, *52*, 4576. Asp, L.; Lindberg, B. *Acta Chem. Scand.* **1950**, *4*, 60. Ioffe, I. S.; Sukhina, A. F. *Zh. Obshch. Khim.* **1953**, *23*, 295; *Chem. Abstr.* **1954**, *48*, 2640d.

H, s, 5-OH); $^{13}$C-NMR δ 15.18, 19.92, 55.65, 57.26, 61.99, 67.20, 82.51, 95.32, 113.08, 116.37, 118.25, 121.60, 133.92, 136.56, 146.46, 149.97, and 152.23; MS *m/z* 286 (74) $(M)^+$, 271 (100). Anal. Calcd for $C_{17}H_{18}O_4$: C, 71.31; H, 6.34. Found: C, 71.21; H, 6.23.

**5,7,8-Trimethoxy-3-methyl-2-propargyl-1,4-naphthoquinone (14).** (a) A mixture of naphthol **13** (143 mg; 0.500 mmol) in $CH_3CN$ (50 mL) and ceric ammonium nitrate 1.15 g (4 equiv) in $H_2O$ (11.5 mL) was stirred at rt (20 min), poured into $H_2O$ (100 mL), and extracted with $CHCl_3$ (3 × 100 mL). Separation of the crude product by chromatography (dry column) ($Et_2O$–$C_6H_6$) (1:1)) provided naphthoquinone **14** (119 mg; 80%), mp 182.0–182.5 °C ($C_6H_6$–ligroine).

(b) The oxidation of naphthol **13** (143 mg; 0.500 mmol) by [bis(trifluoroacetoxy)iodo]benzene (473 mg; 1.10 mmol) in a mixture of $CH_3CN$ (60 mL) and $H_2O$ (30 mL) at 0 °C (4 h) and under $N_2$ also gave naphthoquinone **14** (64 mg; 43%); IR $\nu_{max}$ (KBr) 3240, 2100, 1645 cm$^{-1}$; $^1$H-NMR δ 1.94 (1 H, t, *J* = 2.7 Hz, 3′-H), 2.16 (3 H, s, 3-$CH_3$), 3.43 (2 H, d, *J* = 2.7 Hz, 1′-H), 3.83 (3 H, s, 7-$OCH_3$), 3.93 (6 H, s, 5,8-$OCH_3$), and 6.69 (1 H, s, 6-H); $^{13}$C-NMR δ 12.91, 15.79, 56.16, 56.68, 61.34, 68.83, 79.68, 101.14, 113.22, 126.59, 139.94, 143.25, 145.57, 157.63, 159.46, 183.18, and 183.18; MS *m/z* 300 (56) $(M)^+$, 77 (100). Anal. Calcd for $C_{17}H_{16}O_5$: C, 67.99; H, 5.37. Found: C, 68.07; H, 5.53.

**5,7,8-Trimethoxy-3-methyl-2-(2-oxopropyl)-1,4-naphthoquinone (15).** A mixture obtained from naphthoquinone **14** (300 mg; 1.00 mmol) in $CH_3CN$ (30 mL) and Nafion $H^+/Hg^{++}$ beads (1.0 g) in $H_2O$ (1 mL) was stirred at rt (3.5 h), filtered, poured into $H_2O$ (100 mL), and extracted with $CHCl_3$ (3 × 50 mL). The residue of all organic extracts, after chromatography (wet column) (AcOEt–petroleum ether (3:1), bp 35–60 °C), yielded acetonylnaphthoquinone **15** (272 mg; 85%): mp 173.0–173.5 °C ($C_6H_6$–ligroine) (lit.[3] mp 170–171 °C); IR $\nu_{max}$ (KBr) 1720, 1640 cm$^{-1}$; $^1$H-NMR δ 2.03 (3 H, s, 3′-H), 2.27 (3 H, s, 3-$CH_3$), 3.69 (2 H, s, 1′-H), 3.81, 3.95, and 3.96 (3 × 3 H, 3s, 5,7,8-$OCH_3$), and 6.71 (1 H, s, 6-H); $^{13}$C-NMR δ 13.30, 30.16, 41.74, 56.18, 56.72, 61.31, 101.20, 113.39, 126.41, 139.33, 143.26, 146.30, 157.69, 159.33, 183.08, 184.19, and 203.76; MS *m/z* 318 (67) $(M)^+$, 233 (100). Anal. Calcd for $C_{17}H_{18}O_6$: C, 64.14; H, 5.70. Found: C, 63.70; H, 5.76.

**5,8-Dihydroxy-3-methoxy-7-methyl-6-(2-oxopropyl)-1,4-naphthoquinone (Javanicin) (1).** A mixture of naphthoquinone **15** (64 mg; 0.20 mmol) and LiI (90 mg; 0.66 mmol) in *tert*-butyl methyl ketone (20 mL) was heated at reflux for 30 min, allowed to cool to rt, poured into water, and extracted with $CHCl_3$ (3 × 50 mL). The crude product was purified by chromatography (wet column) on deactivated silica gel (AcOEt–petroleum ether (3:1), bp 35–60 °C) and afforded javanicin (**1**) (50 mg; 85%): mp 207.5–208.0 °C (1,2-dichloroethane–ligroine) (lit.[3] mp 207–208 °C); IR $\nu_{max}$ (KBr) 1710, 1600 cm$^{-1}$; $^1$H-NMR δ 2.22 (3 H, s, 3′-H), 2.28 (3 H, s, 7-$CH_3$), 3.88 (2 H, s, 1′-H), 3.92 (3 H, s, 3-$OCH_3$), 6.19 (1 H, s, 2-H), 12.83, and 13.22 (2 × 1 H, 2s, 5,8-OH); $^{13}$C-NMR δ 12.82, 29.98, 41.17, 56.73, 108.35, 109.58, 134.13, 142.44, 159.61, 160.26, 160.56, 161.31, 177.70, 184.35, and 203.74; MS *m/z* 290 (94) $(M)^+$, 248 (100). Anal. Calcd for $C_{15}H_{14}O_6$: C, 62.07; H, 4.86. Found: C, 62.07; H, 4.95.

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