

## QUINONES FROM THE SEEDS OF *IRIS SPURIA* VAR. *HALOPHILA*

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في هذا البحث تم فصل ثلاثة مركبات كينونية من نبات ايرس سيبوريا صنف هالوفيليا. وقد تم التعرف عليها بواسطة صفاتها الطبيعية والكيميائية وطيف الأشعة فوق البنفسجية وطيف الرنين النووي المغناطيسي ومقياس الكتلة. وقد ثبت أنها: بريمين ؛ ديهيدروايريسوكين ؛ و ٢-هيدروكسي، ٣-هيبتا ديسينيل ، ٥-ميثيل ، ٦-هيدروكسي ميثيل ، ٤،١-بنزوكينون.

From the seeds of *Iris spuria* var. *halophila*, 3 quinones were isolated. On the basis of spectroscopic methods and chemical evidence, the quinones were shown to be primin (2-methoxy, 6-pentyl benzoquinone), dehydroirisoquin (2-hydroxy, 3-octadecenyl, 5-methoxy-1,4-benzoquinone) and 2-hydroxy-3-heptadecenyl, 5-methyl, 6-hydroxymethyl, 1,4-benzoquinone.

### INTRODUCTION

*Iris spuria* var. *halophila* (Iridaceae) is a showy decorative plant growing in Egypt<sup>1</sup>. Most of the Irises are cultivated for ornamental purposes, although large number of biologically active compounds have been isolated from different species<sup>2-4</sup>. The study of *Iris* species has provided a large number of flavonoidal compounds<sup>5-7</sup>, mainly isoflavonoids<sup>8-10</sup>, in addition to a number of biologically active benzoquinones<sup>2,11,12</sup>.

In the course of continuous investigations of the constituents in *Iris* species, three benzoquinones have been isolated from the seeds of *Iris spuria* var. *halophila*. Screening of the available current literature showed that 5,7-dihydroxy-6,2'-dimethoxy isoflavone, iristectorigenin A and tectorin A were isolated from the rhizomes of *Iris spuria* grown in India<sup>13</sup>.

### EXPERIMENTAL

Melting points were recorded on Koffler hot stage microscope, type (E.S.P. Boetius M) and are uncorrected. UV spectra were recorded with Unicam SP 800 B recording spectrophotometer. IR spectra were recorded

with Perkin Elmer Infra-red spectrophotometer 720. MS were recorded at 70 eV Kratos MS 50, 300 MHz, Brücker WH for <sup>1</sup>H-NMR using TMS as an internal standard and chemical shifts are given on  $\delta$  (ppm) scale.

Extraction and Isolation: The seeds of *Iris spuria* var. *halophila* cultivated at the Experimental Station of Medicinal Plants, Faculty of Pharmacy, University of Assiut, were collected in August 1991. Air-dried and milled seeds approximately 500 g were extracted with n-hexane at room temp. The extract (60 g) was subjected to CC on silica gel using n-hexane and n-hexane-EtOAc, successively, as eluents. Elution with n-hexane-EtOAc (85:15) gave compound 1. Further elution with n-hexane-EtOAc (80:20 ~ 65:35) gave a mixture of two compounds which were isolated by prep. TLC using silica gel and CHCl<sub>3</sub>-MeOH (7:1) as solvent system to give compound 2 and compound 3 respectively.

Primin (2-methoxy, 6-pentyl 1,4-benzoquinone) 1; orange yellow oil, UV:  $\lambda_{\max}^{\text{MeOH}}$  nm (log  $\epsilon$ ) 265 (2.25), 358 (2.6); IR:  $\nu_{\max}$ (KBr), 3000, 2850, 1660, 1635, 1596 and 1231 cm<sup>-1</sup>; <sup>1</sup>H-NMR (300 MHz, MeOH-d<sub>4</sub>):  $\delta$  0.88 (t, 3H, CH<sub>3</sub>), 1.20 (br.s, 6H, CH<sub>2</sub>), 2.48 (t, 2H, CH<sub>2</sub>-Q), 4.2 (s, 3H, OCH<sub>3</sub>), 5.78 (d, J = 2.5, 1H, H-3) and 6.48 (m, 1H, H-5); MS: m/z (relative

intensity) 208 [ $M^+$ , 98], 194 (18), 181 (10), 167 (5), 153 (100), 138 (20), 125 (30), 123 (16) and 87 (28).

Dehydroirisoquin (2-hydroxy, 3-octadecenyl, 5-methoxy, 1,4-benzoquinone) **2**; violet crystals (MeOH), m.p. 62-64°C; UV  $\lambda_{\max}^{\text{MeOH}}$  nm (log  $\epsilon$ ) 290 (4.2), 350 (2.2); IR  $\nu_{\max}$  (KBr) 3338, 2955, 2910, 2800, 1685, 1655, 1624, 1598, 1233 and 903  $\text{cm}^{-1}$ ;  $^1\text{HNMR}$  (300 MHz, MeOH- $d_4$ ):  $\delta$  0.9 (t, 3H,  $\text{CH}_3$ ), 1.31 (br.s, 24H), 2.05 (br.s, 4H,  $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$ ), 2.35 (t, 2H,  $\text{CH}_2-\text{Q}$ ), 3.8 (s, 3H,  $\text{OCH}_3$ ), 5.31 (t, 2H,  $-\text{CH}=\text{CH}-$ ), 5.78 (s, 1H, H-6) and 7.45 (s, 1H, OH). MS: m/z (relative intensity): 406 [ $M+2$ ] $^+$  (4), 392 (3), 390 (5), 376 (3), 196 (24), 182 (10), 169 (40), 168 (100), 167 (10), 153 (20), 139 (16), 120 (16), 111 (10), 109 (10), 105 (14), 83 (26) and 81 (24).

2-Hydroxy, 3-heptadecenyl, 5-methyl, 6-hydroxymethyl, 1,4-benzoquinone **3**; violet needles (MeOH), m.p. 58-61°C, UV:  $\lambda_{\max}^{\text{MeOH}}$  nm (log  $\epsilon$ ) 258 (4.6) and 310 (2.3); IR:  $\nu_{\max}$  (KBr) 3334, 3310, 2958, 2920, 2810, 1675, 1646, 1622, 1595 and 1210  $\text{cm}^{-1}$ ;  $^1\text{HNMR}$  (300 MHz, MeOH- $d_4$ )  $\delta$  0.9 (t, 3H,  $\text{CH}_3$ ), 1.30 (br.s, 22H), 1.8 (t, 3H,  $\text{CH}_3$ ), 2.0 (4H,  $-\text{CH}_2-\text{CH}=\text{CH}-$ ), 2.4 (t, 2H,  $\text{Q}-\text{CH}_2$ ), 4.4 (q, 2H,  $\text{OHCH}_2-$ ), 5.31 (t, 2H,  $-\text{CH}=\text{CH}-$ ) and 7.25 (br.s OH); MS: m/z (relative intensity) 404 [ $M$ ] $^+$  (38), 390 (8), 378 (4), 182 (100), 168 (20), 153 (45), 139 (8), 125 (17) and 97 (10).

## RESULTS AND DISCUSSION

The n-hexane extract of the seeds of *Iris spuria* var. *halophila* was chromatographed on silica gel CC to give quinones **1**, **2** and **3**. The MS of **1** exhibited [ $M^+$ ] at m/z 208 for  $\text{C}_{12}\text{H}_{16}\text{O}_3$  consistent with a benzoquinone substituted with a methoxy and a pentyl group. The base peak at m/z 153 (M-55) is attributed to a dihydroxymethoxytropylium ion formed by cleavage at the benzyl position and rearrangement<sup>17</sup>. Strong IR absorption band in the region of 2850-3000  $\text{cm}^{-1}$  indicated the presence of an alkyl side chain which was determined from both the  $^1\text{HNMR}$  and MS to be n-pentyl fraction. The orientation

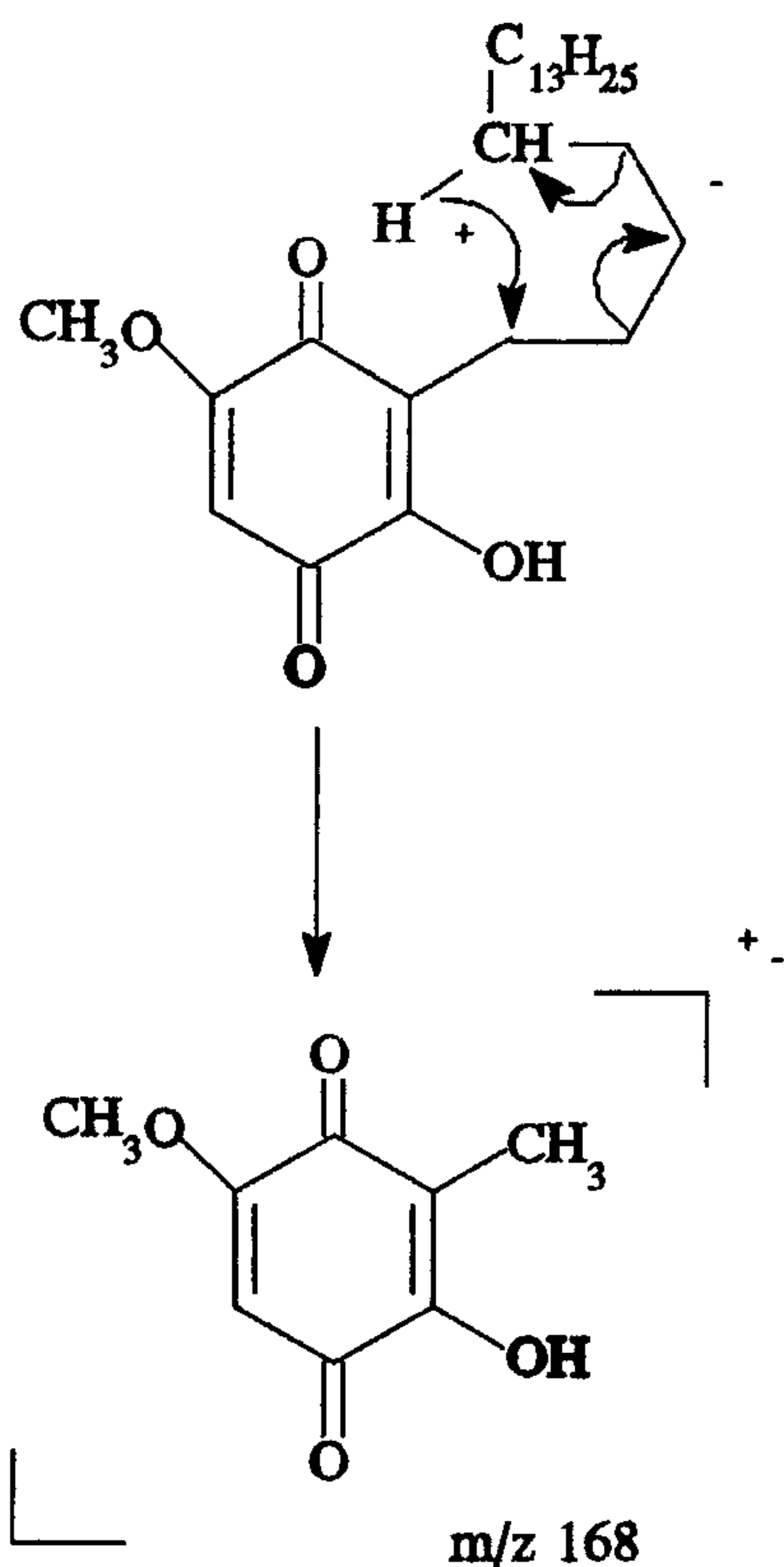
of the two substituents is confirmed by the  $^1\text{HNMR}$  which shows a multiplet at  $\delta$  6.48 obviously coupled with a doublet at  $\delta$  5.78 ( $J=2.5$ ) arising from the two ring protons, indicating that they occupy the 3 and 5 positions (m-position). The data obtained for this compound, suggest that it must be 2-methoxy, 6-n-pentyl-1,4-benzoquinone (primin) previously isolated from *Primula obconica* Hance<sup>14</sup>.

MS of compound **2** gave [ $M+2$ ] $^+$  at m/z 406 indicated a molecular formula  $\text{C}_{25}\text{H}_{40}\text{O}_4$ . The 1,4-benzoquinone moiety was revealed by its IR spectrum which showed bands at 1685, 1655, 1624 and 1598  $\text{cm}^{-1}$ <sup>15</sup> and its UV spectrum with absorption bands at  $\lambda_{\max}^{\text{MeOH}}$  290 (4.2), 350 (2.2)<sup>16</sup>.

Moreover, the IR spectrum revealed the presence of a long aliphatic side chain and a characteristic band at 903  $\text{cm}^{-1}$  indicating the presence of a benzoquinone with one or more isolated carbon atoms on the ring<sup>16</sup>. The presence of a methoxy group was indicated by a strong absorption band at 1233  $\text{cm}^{-1}$  and  $^1\text{HNMR}$  signal at 3.8 ppm (3H). The  $^1\text{HNMR}$  (300 MHz, MeOH- $d_4$ ) showed signals at  $\delta$  5.31 (t, 2H,  $-\text{CH}=\text{CH}-$ ), 2.05 (br.s, 4H,  $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$ ) and 2.35 (t, 2H,  $-\text{CH}_2-\text{Q}$ ). Further, a triplet signal for methyl protons at  $\delta$  0.90 ppm and a broad signal at  $\delta$  1.31 (representing 24 protons) revealed an octadecenyl side chain attached to the quinone moiety. A singlet at  $\delta$  5.78 ppm arising from the ring proton and a broad exchangeable signal at  $\delta$  7.45 (1H) together with the methoxy signal at  $\delta$  3.8 supported the attachment of a hydroxy group at C-2, an octadecenyl group at C-3 and a methoxyl at C-5 to the benzoquinone ring. A trisubstituted 1,4-benzoquinone skeleton was also supported by a strong peak at m/z 168 (base peak), correlates with the quinone fragment that is formed by the loss of heptadecenyl side chain from **2** (Scheme I)<sup>12</sup>.

From these results, it is concluded that compound **2** is dehydroirisoquin (2-hydroxy, 3-octadecenyl, 5-methoxy-1,4-benzoquinone).

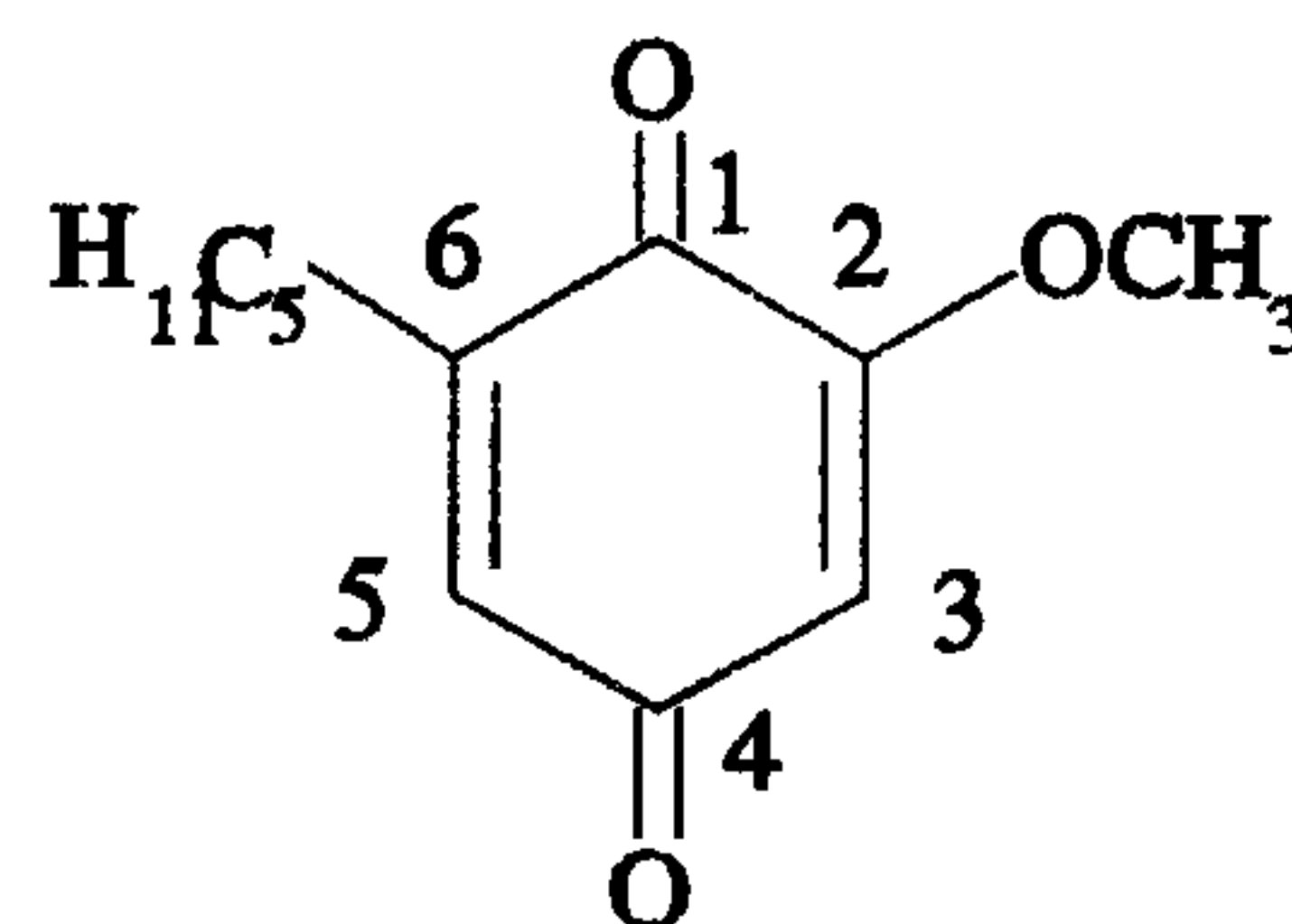
Irisoquin (2-hydroxy, 3-octadecyl, 5-methoxy-1,4-benzoquinone) was isolated from *Iris missouriensis*<sup>12</sup>.



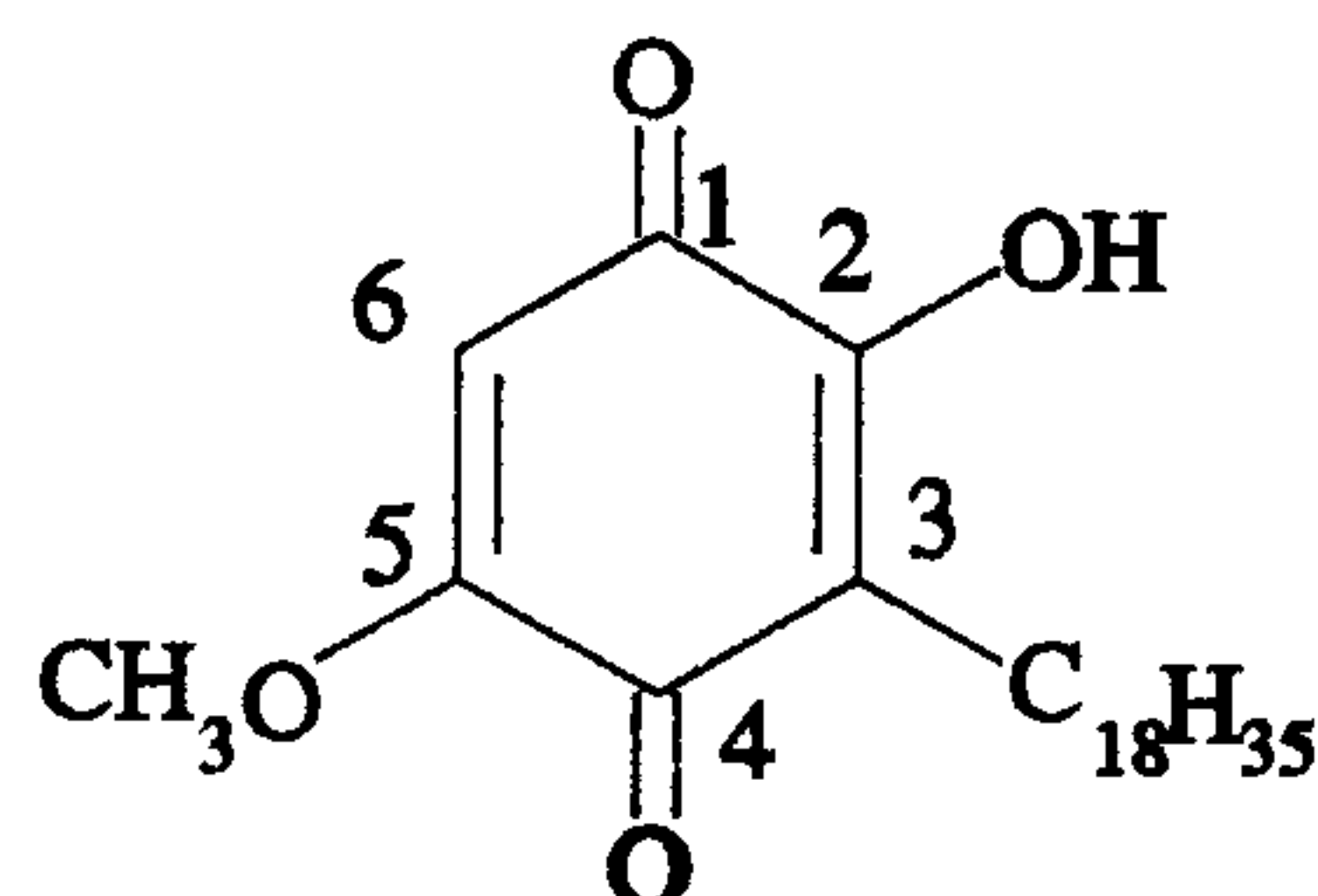
Scheme I

Compound 3 analysed for  $C_{25}H_{40}O_4$  ( $m/z$  404  $[M]^+$ ). It showed UV maxima (MeOH) at 258 (4.6) and 310 (2.3) nm, consistent with the structure of 1,4-substituted benzoquinone chromophore and IR bands (KBr) at 1675, 1646, 1622 and 1595  $cm^{-1}$  characteristic for the conjugated carbonyls and  $C=C$  of a benzoquinone<sup>12</sup>, moreover, the IR spectrum revealed the presence of a long aliphatic side chain. In the  $^1H$ NMR spectrum (300 MHz, MeOH- $d_4$ ), a triplet centered at  $\delta$  1.8 (3H) coupled to a quartet at 4.4 (2H) indicates homoallylic coupling between a methyl and a methylene group<sup>17</sup>. Further, a triplet signal for methyl protons (3H) at  $\delta$  0.9, a triplet signal for the methylene protons adjacent to the quinonoid ring at  $\delta$  2.4 (2H), a broad signal centered at  $\delta$  1.30 (22H), a triplet at  $\delta$  5.31 (2H,  $-CH=CH-$ ) and a broad signal at  $\delta$  2.0 (4H,  $-\underline{CH}_2-\underline{CH}=\underline{CH}-\underline{CH}_2-$ ) revealed a heptadecenyl side chain attached to the quinone moiety. A tetra-substituted 1,4-benzoquinone was also supported by a strong peak at  $m/z$  182 ( $B^+$ base peak), this

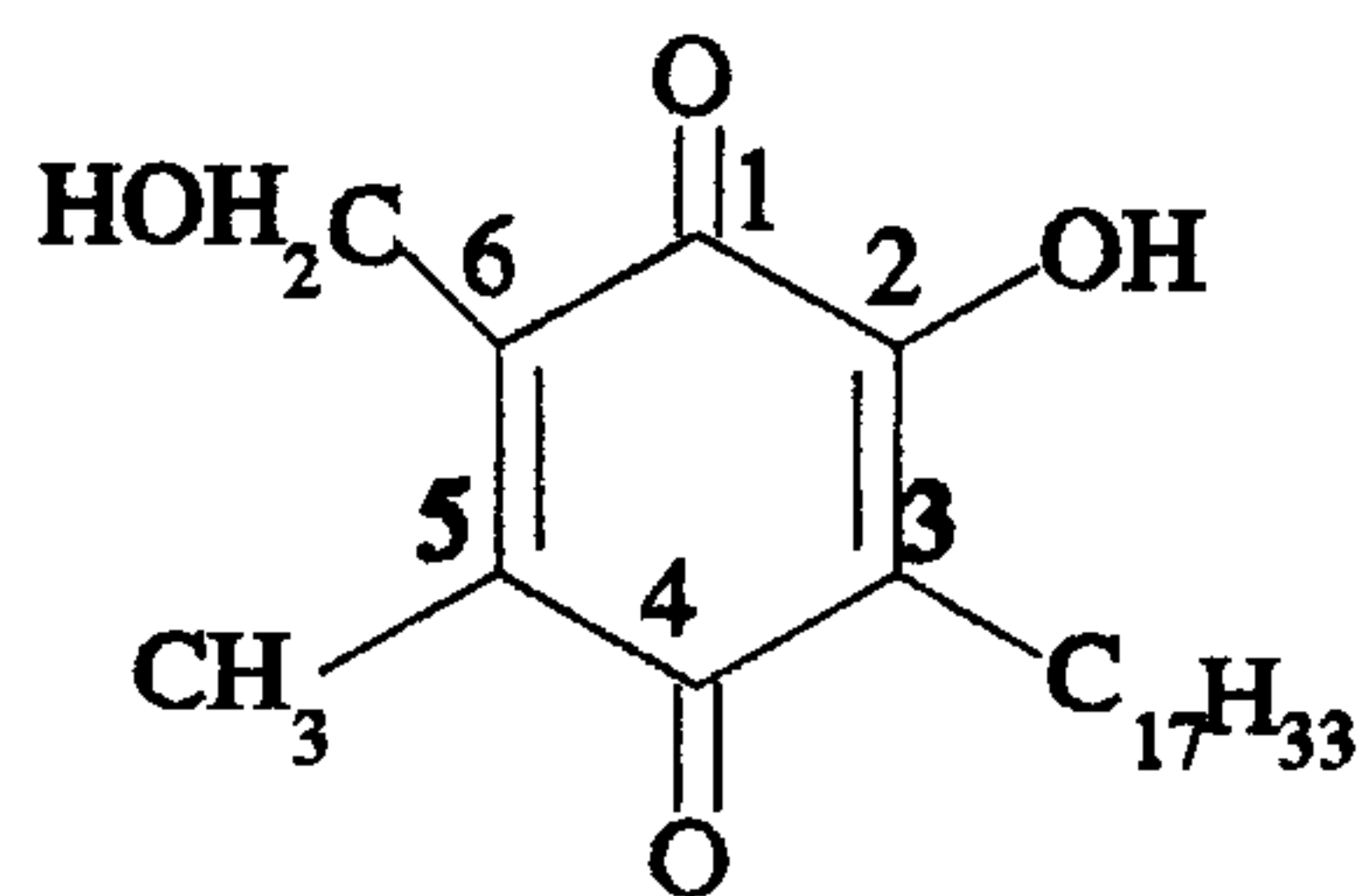
correlates with the quinone fragment and the adjacent methyl group of the side chain<sup>12</sup>. Peaks at  $m/z$  390, 376 and 362 are attributed to the loss of  $CH_2$  from the side chain and characteristic peaks at  $m/z$  168 [ $B^+-CH_2$ ], 153 [ $B^+-CH_2-CH_3$ ] and 139 [ $B^+-CH_2-CH_3-CH_2$ ]. Hence, the structure of 3 was established to be 2-hydroxy, 3-heptadecenyl, 5-methyl, 6-hydroxymethyl, 1,4-benzoquinone.



Comp. 1: Primin (2-methoxy, 6-pentyl, 1,4-benzoquinone)



Comp. 2: Dehydroirisoquin (2-hydroxy, 3-octadecenyl, 5-methoxy, 1,4-benzoquinone)



Comp. 3: 2-Hydroxy, 3-heptadecenyl, 5-methyl, 6-hydroxymethyl, 1,4-benzoquinone

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