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## A new alkylated benzoquinone from rhizomes of *Iris kumaonensis*

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A novel alkylated unsaturated *p*-benzoquinone designated as 3-[(z)-12'-heptadecenyl]-2-hydroxy-5-methoxy-1,4-benzoquinone was isolated from hexane extract of the rhizomes of *Iris kumaonensis* and its structure was confirmed by extensive spectroscopic analysis, IR, MS, HREIMS, 1D, 2D NMR and comparison with the literature data of known compounds.

**Keywords:** *Iris kumaonensis*; Iridaceae; Rhizomes; Unsaturated benzoquinone

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### 1. Introduction

*Iris kumaonensis* Wall ex Don. V. Latham (*Iridaceae*) is a decorative household perennial herb growing wild in the western Himalayas from Kashmir to Uttaranchal at an altitude of 2500–4000 m. Rhizomes of this plant are used for fever [1] and roots are used for kidney infection [2]. The genus *Iris* consists of about 300 species and is distributed throughout the world. About 12 species are found in India [2]. *Iris* species are known to be rich in isoflavonoids, flavonoids [3,4] and quinones [5]. Earlier, we reported six new alkylated benzoquinones, irisoquin-A, irisoquin-B, irisoquin-C, irisoquin-D, irisoquin-E, irisoquin-F and a known benzoquinone irisoquin from the hexane extract of *I. kumaonensis* [6]. During our ongoing research for characterization and identification of new secondary metabolites from western Himalayan flora, we report the isolation and characterization of a novel alkylated unsaturated *p*-benzoquinone. The identification of this compound was carried out by spectral analysis (IR, HREIMS, <sup>1</sup>H and <sup>13</sup>CNMR) and also by comparing with the literature, data of known compounds. This class of compounds are reported to have cytotoxic activity [5].

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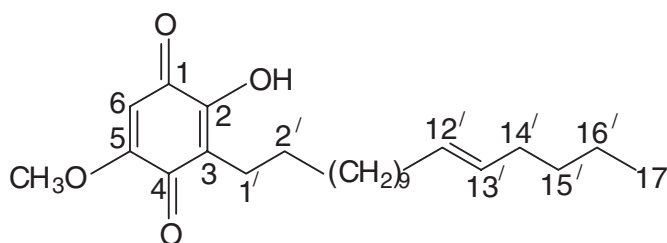
## 2. Results and discussion

Hexane extract of rhizomes of *I. kumaonensis* on repeated column chromatography on silica gel, afforded an orange coloured powder, which was homogenous on TLC. It showed  $[M]^+$  ion at 390.2781 in its HREIMS corresponding to the molecular formula  $C_{24}H_{38}O_4$ . The base peak at  $m/z$  168 [7] showed that compound **1** has 3-alkyl-2-hydroxy-5-methoxy-1,4-benzoquinone moiety [8] which was further supported by its IR spectra indicating the presence of hydroxy and methoxy groups ( $3350$  and  $1225\text{ cm}^{-1}$ ) and conjugated carbonyls of trisubstituted benzoquinone ( $1685$ ,  $1645$  and  $1600\text{ cm}^{-1}$ ) [9]. The  $300\text{ MHz } ^1\text{H NMR}$  spectrum showed a singlet at  $\delta$  5.84 (s, 1H) for quinoid proton,  $\delta$  5.35 (m, 2H,  $-\text{CH}=\text{CH}-$ ) for methine protons of alkyl side chain attached to quinone ring,  $\delta$  3.86 (s, 3H,  $-\text{OCH}_3$ ) and  $\delta$  7.23 (br, s,  $-\text{OH}$ )  $\text{D}_2\text{O}$  exchangeable,  $\delta$  2.46 (t, 2H) for methylene protons of side chain attached to ring,  $\delta$  1.98 (m, 4H) for methylene proton adjacent to olefinic double bond,  $\delta$  1.25 (br s,  $24 \times \text{CH}_2$ ) and  $\delta$  0.92 ppm (t,  $3\text{CH}_3$ ) for terminal methyl of long alkyl side chain.  $^1\text{H}$  and  $^{13}\text{C NMR}$  data are provided in table 1. The position of methoxy group at  $\delta$  3.86 ppm was confirmed by NOE experiment. The methoxy protons  $\delta$  3.86 ppm showed NOE on the proton at  $\delta$  5.84 ppm indicating the  $-\text{OCH}_3$  and quinoid proton attached on 5 and 6 positions of the quinoid ring. The position of the OH, OMe and alkyl side chain was finally confirmed by HMBC (figure 1). These data were identical with the reported data of irisoquin A–F reported by us earlier [6], except that **1** had a double bond in the side chain which was evident from a 2H proton triplet at  $\delta$  5.35 ( $J=4.94$ ) in its  $^1\text{H NMR}$ , while the corresponding signals which appeared at  $\delta$  130 in its  $^{13}\text{C NMR}$  are very similar to that reported for maesanin [8] and other quinones which have a double bond at  $n-5$  position [8–10], but differ from our compound in having two more carbon in the side chain.

The absence of the characteristic IR absorption band at  $950\text{ cm}^{-1}$  [11] ruled out the possibility of a *trans* double bond between  $C'-12$  and  $C'-13$ . However, a prominent

Table 1.  $^1\text{H}$  (300 MHz) and  $^{13}\text{C NMR}$  (75 MHz) data of compound **1** in  $\text{CDCl}_3$ .

No.	$\delta$ $^1\text{H}$	$\delta$ $^{13}\text{C}$
1	–	183.2
2	–	151.9
3	–	119.6
4	–	182.1
5	–	161.5
6	5.84 (s)	102.5
1'	2.46	23.03
2'	1.45	28.4
3'–10'	1.25 (br s)	29.3–29.9
11'	1.98	27.6
12'	5.35	130.3
13'	5.35	130.3
14'	1.98	28.4
15'	2.0	32.3
16'	2.02	23.09
17'	0.92	14.53
$\text{OCH}_3$	3.86	57.16
OH	7.23	–



Compound 1.

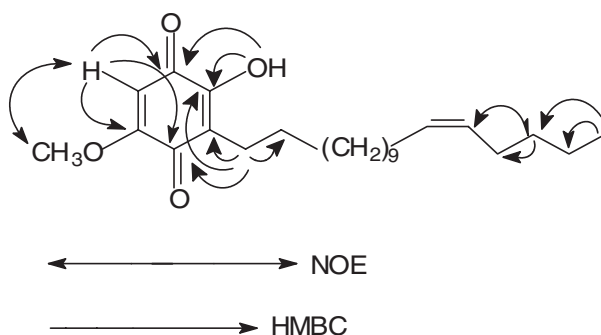


Figure 1. HMBC and NOE correlation of compound 1.

band at  $1636\text{ cm}^{-1}$  assigned a *cis* double bond which was further confirmed by HMBC correlation of signals at 27.6 and 28.4 ppm in the side chain indicating a double bond between C-12' and C-13'.

### 3. Experimental

#### 3.1. General experimental procedures

Melting points were recorded on a Mettler FP800 (central processor) and are uncorrected. IR spectra were measured on a JASCO FT/IR 5300, 1D and 2D NMR were recorded in  $\text{CDCl}_3$  on a Bruker DRX-300 MHz ( $^1\text{H}$ ) and 75 MHz ( $^{13}\text{C}$ ) instrument using TMS as the internal standard. EIMS and HREIMS were recorded on Finnigan MAT 8230, 600 mA, 3 kV mass spectrometer. Column chromatography was carried out on silica gel-H (without binder), silica gel (60–120 mesh) and TLC on silica gel-G (Merck).

#### 3.2. Plant material

The rhizomes of *I. kumaonensis* were collected from Koksar area of Lahual-spiti district at a height of 3200 m in Himachal Pradesh, India, during September 2003. An authenticated voucher specimen has been deposited in the herbarium of our institute.

### 3.3. Extraction and isolation

Five hundred grams of air dried powdered rhizomes of *I. kumaonensis* were extracted with hexane, chloroform, acetone, methanol (each 5 × 500 mL) at room temperature (22–25°C). The solvent was removed under reduced pressure yielding 10, 18, 20 and 23 g extracts, respectively.

Eight grams of hexane extract was subjected to dry column chromatography (70 mm diameter) over silica gel-H (without binder) and eluted with hexane and increasing amount of 1, 2, 5, 10, 25 and 50% ethyl acetate and finally eluted with 5% methanol in ethyl acetate, 1–2% ethyl acetate in hexane fraction afforded an orange colour gum, (2.0 g) which was a mixture of five compounds and rechromatographed over silica gel (60 g) and eluted with CH<sub>2</sub>Cl<sub>2</sub>. Fractions 5–20 (25 mL each) were pooled together and on removal of the solvent, an orange coloured viscous liquid compound **1** (80 mg), which was homogeneous on TLC plate was isolated. Further elution with 1% ethyl acetate in CH<sub>2</sub>Cl<sub>2</sub>, fractions 28–29 afforded a white powder (75.0 mg) which on Co-TLC, m.p. and literature data was identified as β-sitosterol.

**3-[(z)-12'-Heptadecenyl]-2-hydroxy-5-methoxy-1,4-benzoquinone.** Orange coloured powder, m.p. 70.3°C, IR (KBr)  $\nu_{\max}$  3345, 2960, 2925, 1680, 1636, 1600, 1220 and 1210 cm<sup>-1</sup> for <sup>1</sup>H and <sup>13</sup>C NMR (see table 1), HREIMS *m/z* 390.2781 (calculated for C<sub>24</sub>H<sub>38</sub>O<sub>4</sub>, 390.2770) *m/z* (rel. int.) 390 (12.5), 365 (10.48), 364 (41.72), 125 (10.7), 111 (11.45), 182 (5.6), 168 (100), 83 (27.98), 69 (54.9), 55 (74.4), 43 (83.4) and 41 (74.9).

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