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A NAPHTHOQUINONE FROM *HELICTERES ANGUSTIFOLIA*

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Key Word Index—*Helicteres angustifolia*; Sterculiaceae; helicquinone; 2,3-dihydro-8-hydroxy-3,5,6-trimethyl naphtho(2,3-b)furan-4,9-dione.

Abstract—A new naphthoquinone named helicquinone has been isolated from the roots of *Helicteres angustifolia*, and its structure was found to be 2,3-dihydro-8-hydroxy-3,5,6-trimethylnaphtho(2,3-b)furan-4,9-dione on the basis of spectroscopic evidence.

INTRODUCTION

The roots of *Helicteres angustifolia* L., which grows on hills in the Guangxi Province of China, have been used as one of the traditional drugs for the treatment of flu. In a previous communication, we reported that three new triterpenoids, methyl helicterilate, methyl helicterate and helicterilic acid, had been obtained from this plant together with three known compounds, sitosturol, betulic acid and oleanolic acid [1]. During further studies on the same species, we isolated additionally a new naphthoquinone derivative named helicquinone, which we consider to be 2,3-dihydro-8-hydroxy-3,5,6,-trimethylnaphtho(2,3-b)furan-4,9-dione.

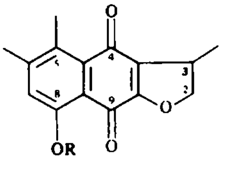
RESULTS AND DISCUSSION

Helicquinone (**1**) was easily decolourized by lithium aluminium hydride and the reduced product was readily oxidized by air, the behaviour indicating a quinone [2]. The UV, IR [3190 (chelated hydroxyl), 1670 (carbonyl), (1620 cm^{-1} (chelated carbonyl)] and ^{13}C NMR (two carbonyl, two vinyl, six aromatic and five aliphatic carbons) spectra showed that it could be a naphthoquinone of the juglone type bearing five aliphatic carbons [3, 4]. The mass spectrum showed *m/z* 258.0791 $[M]^+$ ($C_{15}H_{14}O_4$), 243 $[M - Me]^+$ and 230 $[M - CO]^+$ (base peak). In the ^{1}H NMR spectrum (DMSO-d_6, 60 MHz), a signal at δ11.60 was assignable to the hydroxyl proton at C-8 [5]; signals at δ6.73 (1H, *s*), 2.48 (3H, *s*) and 1.81 (3H, *s*) were assigned to an aromatic proton at C-7 and two methyl groups at C-6 and C-5, respectively. The locations of the above groups were confirmed by examining the NOE of the relevant protons. On irradiation at δ2.48 (methyl group at C-6), the intensity of the signal at 6.73 (proton at C-7) increased by 20%. The hydroxyl group of helicquinone was methylated to form helicquinone methyl ether (**2**), in which the ^{1}H NMR signal of the aromatic proton was shifted downfield by 0.27 ppm (δ6.73–7.00). On irradiating the signal (δ3.95) of the methoxyl protons in helicquinone methyl ether, the intensity of the signal for the aromatic proton at δ7.00 increased by 22%. We have determined that two of the aliphatic carbons in helicquinone are attached to the aromatic ring as methyl groups, and the other three should exist as Me–CH–CH_2–O– and be attached to the quinone ring in accordance with proton spin-decoupling experiments. On decoupling the methylene protons at δ4.35 (2H, *m*), the signal for CH at 3.23 (1H, *m*) simplified to a quartet ($J = 7.2$ Hz). In turn, on decoupling the methine proton, the signal for the methyl group at δ1.22 (3H, *d*, $J = 7.2$ Hz) simplified to a singlet and the CH_2 changed to a double-doublet. On the basis of the above spectroscopic evidence, the structure of helicquinone could be assigned to **1** or **3**.

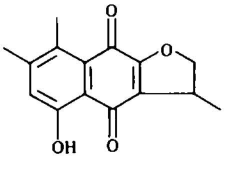
Lillie and Musgrave found that the chemical shift of the 5-hydroxyproton of 5-hydroxy-1,4-naphthoquinones Juglone-type naphthoquinones) is generally influenced by substituents such as hydroxy, methyl, chloro and bromo groups, and the effects caused by these substituents are additive. Thus, the chemical shift of the 5-hydroxy proton can be calculated according to the contributions of different substituents [6]. By extending Musgrave's findings, to methoxy derivatives, Inoue *et al.*, using the hydroxyproton shift of juglone (δ11.87) as the base value, calculated the contributions of the methoxyl or alkoxy group at C-2 and C-3 to be + 0.33 and − 0.19 respectively [7]. Regarding the structures of **1** and **3**, the calculated chemical shifts of the hydroxy-proton are δ11.74 and 12.34, respectively. The effect of the aromatic methyls on δ_{OH} is ignored, and it is assumed that the effect of the Me CHCH$_2$O– system is equivalent to the effect of Me and MeO.

1 $\delta_{OH} = 11.87 + 0.06\ (2\text{-Me}) - 0.19\ (3\text{-OMe}) = 11.74$

2 $\delta_{OH} = 11.87 + 0.14\ (3\text{-Me}) + 0.33\ (2\text{-OMe}) = 12.34.$



1 R = H
2 R = Me



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As helicquinone is insoluble in chloroform, its ^1H NMR spectrum was recorded in DMSO-d_6, in which the signals for hydroxyl groups usually appear more downfield than in $CDCl_3$. We noticed that the chemical shift (δ 11.60) for the hydroxy-proton is very close to that calculated for **1** and, if recorded in $CDCl_3$, it would probably appear at higher field and still be closer to that of **1** than to that of **3**. It is concluded that the probable structure of helicquinone is 2,3-dihydro-8-hydroxy-3,5,6-trimethylnaphtho(2,3-b)furan-4,9-dione.

EXPERIMENTAL

Extraction and isolation. Dried roots of *H. angustifolia* (10 kg) were extracted with EtOH, and the EtOAc-soluble portion of the extracts was packed on top of a silica gel (100 g, 120–160 mesh) column, and eluted with cyclohexane–EtOAc. The fraction (2 g) obtained using a 2 : 1 solvent mixture was a red powder which was treated by flash CC on silica gel (1 kg pressure on top), and the fraction of the red band eluted with $CHCl_3$–Me_2CO (10 : 1) was crystallized (MeOH) to give helicquinone (0.25 g).

Helicquinone (**1**). Red crystals, mp 360°; UV λ_{max}^{MeOH} nm ($\log \varepsilon$): 221 (4.22), 266 (4.24), 274 (4.33), 298 (4.04), 390 (3.93); IR ν_{max}^{KBr} cm^{-1}: 3190, 2970, 2930, 1670, 1620, 1560, 1450, 1425, 1380, 1358, 1320, 1260, 1225, 1185, 1160, 950; MS m/z (rel. int.): 258.0791 $[M]^+$ (24) ($C_{15}H_{14}O_4$ requires: (258.0891), 243.0671 (18) ($C_{14}H_{11}O_4$ requires: 243.0656), 230.0939 (100) ($C_{14}H_{14}O_3$ requires: 230.0943), 215 (34), 202 (8), 187 (4), 159 (9), 158 (15), 128 (4), 115 (5), 91 (3), 83 (4); ^{13}C NMR (DMSO-d_6, 15 MHz): δ 178.9 (*s*), 179.5 (*s*), 161.0 (*s*), 158.9 (*s*), 144.1 (*s*), 127.7 (*s*), 124.8 (*s*), 118.9 (*d*), 118.9 (*s*), 114.5 (*s*), 75.1 (*t*), 25.7 (*d*), 22.4 (*q*), 16.9 (*q*), 7.8 (*q*).

Helicquinone methyl ether (**2**). Compound **1** (150 mg), freshly prepared Ag_2O (200 mg) and MeI (5 ml) in 30 ml dry Me_2CO were heated on a steam bath. After 7 hr reflux the mixture was cooled and filtered. The filtrate was evaporated and the residue was packed on top of a silica gel column and eluted with $CHCl_3$–Me_2CO (20 : 1). The fraction containing the desired product was crystallized (MeOH) to give **2**, mp 280°. ^1H NMR (DMSO-d_6, 60 MHz): δ 7.00 (1H, *s*), 4.36 (2H, *m*), 3.95 (3H, *s*), 3.23 (1H, *m*), 2.57 (3H, *s*), 1.82 (3H, *s*), 1.22 (3H, *d*, $J = 7.3$ Hz).

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