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Stereochenols A and B, two quinones from *Stereospermum chelonoides*

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Abstract

Two quinones, stereochenols A (**1**) and B (**2**) were isolated from a methanol extract of the stem bark of *Stereospermum chelonoides*, in addition to the known naphthoquinones, sterekunthal B (**3**) and sterequinone C (**4**). The structures of these compounds were established by extensive spectroscopic analyses and by comparison of their spectral data with those of related compounds.

Keywords: *Stereospermum chelonoides*; Bignoniaceae; Sterekunthal B; Sterequinone C; Anthrakunthone; Stereochenol

1. Introduction

Stereospermum chelonoides DC. (Syn. *S. suaveolens*; Bengali name- Atkapali, Paruli gachh; Family-Bignoniaceae) is a medium-sized tree, distributed in the subhimalayan tract and outer hills, central India, western Peninsula, Burma, Bangladesh and the English Forest. It is reputed for its antipyretic property and is also useful in excessive thirst, cough and asthma (Ghani, 1998). Lapachol (Rao et al., 1968), dinatin, dinatin-7-glucuroniside and β-sitosterol (Subramanian et al., 1972) have previously been reported from this plant. Our studies with *S. chelonoides* provided a new anthraquinone, stereochenols A (**1**) and a new naphthoquinone, stereochenol B (**2**) along with sterekunthal B (**3**) and sterequinone C (**4**), previously known from *S. kunthianum* (Onegi et al., 2002) and *S. personatum* (Kumar et al., 2003).

2. Results and discussion

Extensive chromatographic separation and purification of a methanol extract of the stem bark of *S. chelonoides*, led to the isolation of two new quinones which we established to be stereochenol A (**1**) and stereochenol B (**2**) along with the known naphthoquinones, sterekunthal B (**3**) and sterequinone C (**4**), which were identified by comparison of their physical and spectral data with previously reported values (Onegi et al., 2002; Kumar et al., 2003).

The electrospray mass spectrum of compound **1** showed a pseudo molecular ion $[M+H]^+$ peak at *m/z* 293 corresponding to the molecular formula $C_{19}H_{16}O_3$. This was 16 mass unit lower than that of anthrakunthone (**5**) (*m/z* 308, $C_{19}H_{16}O_4$) previously reported from *S. kunthianum* (Onegi et al., 2002). The ^{1}H NMR spectrum of **1** displayed a total of 6 aromatic proton resonances. The doublets ($J = 8.0$ Hz), each integrating for one proton, centered at δ 7.58 and 8.18 could be assigned to the *ortho* coupled protons at C-12 and C-11, respectively. The broad doublets ($J = 7.5$ Hz) centered at δ 7.77 and 8.25, each of two proton intensity, were ascribed to the four aromatic ring protons, H-4 and H-5 and H-3 and H-6, respectively. The ^{1}H NMR spectral data also revealed two three proton singlets at δ 2.19 and 2.79 assignable to the side chain methyl linked to C-13 and aromatic methyl at C-17, respectively. The vicinal methylenes protons appeared as triplets ($J = 7.5$ Hz) at δ 2.77 and 3.10. Considering the chemical shifts, the relatively downfield signal at δ 3.10 was attributed to the benzylic methylene (H_2-15), while that at δ 2.77 could be

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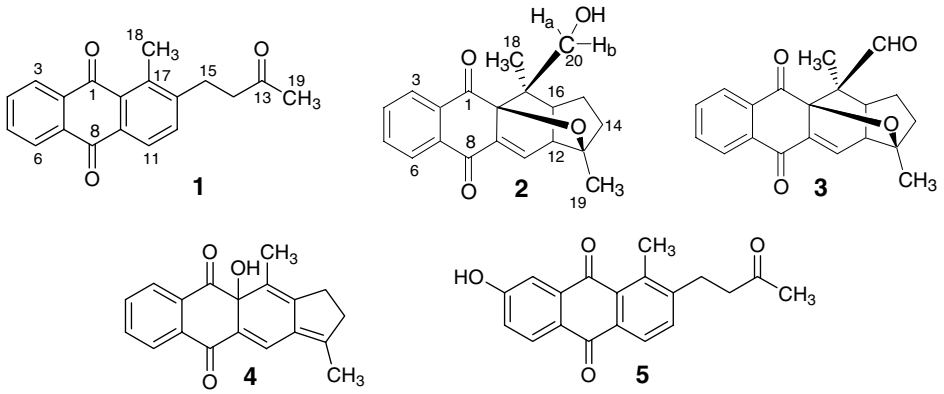
assigned to H_2-14, by default. The above spectral feature was in close agreement to that published for anthrakunthone (Onegi et al., 2002), which has a hydroxyl function at C-4 (**5**). On this basis, compound **1** was characterized as 4-deoxyanthrakunthone, for which we propose the trivial name stereochenol A.

The molecular formula of quinone **2** was established as $C_{20}H_{20}O_4$ by electrospray mass spectral measurement. This was 2 atomic mass unit higher than that of stere-



kunthal B (**3**) (*m/z* 322, $C_{20}H_{18}O_4$). The ^{1}H NMR spectrum of compound **2** was almost identical to that of sterekunthal B(**3**) previously known to occur in *S. kunthianum* (Onegi et al., 2002) and *S. personatum* (Kumar et al., 2003). This suggested a close structural similarity between these two compounds. However, the aldehydic proton signal observed at δ 10.27 in the ^{1}H NMR spectrum of sterekunthal B (**3**) was absent from the spectrum of **2**. Rather the ^{1}H NMR spectrum of **2** showed an AB quartet ($J = 7.5$ Hz) centered at δ 3.78 and 4.28 (each 1H) assignable to a hydroxymethyl (–CH_2OH) group protons. This demonstrated that the aldehydic functionality (–CHO) in sterekunthal B (**3**) was replaced by a hydroxymethyl group (–CH_2OH) in **2**. The ^{1}H NMR spectral data of **2** revealed the presence of five aromatic proton resonances at δ 7.53 (1H, d, $J = 7.8$ Hz), 7.47 (1H, dt, $J = 1.2$, 7.0 Hz), 7.68 (1H, dt, $J = 1.2$, 7.8 Hz), 7.90 (1H, dd, $J = 7.8$, 1.2 Hz) and 8.10 (1H, dd, $J = 7.8$, 1.2 Hz). In the ^{1}H–^{1}H COSY experiment, the proton at δ 8.10 showed strong coupling with a proton at δ 7.47, which in turn, revealed coupling with the proton resonating at δ 7.68. The latter proton also exhibited strong interaction with the proton appeared at δ 7.90. This coupling pattern was consistent with a 1,2-disubstituted aromatic nucleus. The remaining proton at δ 7.53 (H-11) showed coupling with another proton at δ 2.96 (1H, dd, $J = 4.2$, 7.0 Hz, H-12) which also demonstrated further correlation to a proton at δ 1.85 (1H, m, H-16) in the COSY. The relatively weak coupling (4.2 Hz) between H-12 and H-16 established a *cis*-configuration between these two protons. In the COSY H-16 showed additional correlation with a two proton multiplets at δ 1.91–1.93 (H_2-15), which is in turn, exhibited interaction with a multiplets at δ 1.58 (H_2-14), thus completing the spin system. The remaining two singlets, each of three proton intensity, at δ 0.55 and 1.19 could be assigned to the methyl group protons at C-17 and C-13, respectively. On this basis, the structure of compound **2** was established as reduced sterekunthal B (**3**), for which the trivial name stereochenol B (**2**) has been proposed.

3. Experimental

3.1. General

Vacuum liquid chromatography was performed on silica gel (70–230 mesh). ^{1}H NMR spectra were acquired using Ultra Shield Bruker DPX 300 NMR instrument. The ^{1}H NMR spectra were acquired in $CDCl_3$ and chemical shifts are reported in ppm with respect to residual non deutarated solvent signal. Mass spectra were recorded on a JEOL DX-300 spectrometer. All solvents were of analytical grade.

3.2. Plant material

Stem bark of *S. chelonoides* was collected from Chittagong in the month of August 2004. The plant was identified by Mrs. Mahmuda Begum, Senior Scientific officer at Bangladesh National Herbarium, Dhaka, where a voucher specimen has been deposited for this collection (accession number: 387, 25546).

3.3. Extraction and isolation

The sun dried bark (533 g) was powdered and extracted with methanol (1.5 L). The solvent was evaporated under reduced pressure in a rotary evaporator to obtain a gummy residue (5 g) and was subjected to fractionation by using the modified Kupchan partitioning (Van Wagenen et al., 1993) method into *n*-hexane, carbon tetrachloride, chloroform and aqueous soluble

fractions. Evaporation of solvent afforded *n*-hexane (1.5 g), carbon tetrachloride extract (0.04 g), chloroform (2.54 g) and aqueous soluble materials (0.92 g). The *n*-hexane and chloroform soluble partitionates were separately chromatographed over silica gel (Kiesel gel 60H, mesh 70–230) and the column was eluted with *n*-hexane followed by mixtures of *n*-hexane and ethyl acetate in order of increasing polarities. The fraction eluted with 25% ethyl acetate in *n*-hexane from chloroform solubles were collected, concentrated and rechromatographed over silica gel to obtain compound **1** (1.5 mg) and **2** (2.3 mg) in pure form. In the same manner, the materials eluted with 20–25% ethyl acetate in *n*-hexane from the *n*-hexane solubles and the fraction eluted with 22.5% ethyl acetate in *n*-hexane from the chloroform soluble materials were collected, concentrated and rechromatographed over silica gel separately to obtained compound **3** (2 mg) and **4** (3.5 mg), respectively.

3.4. Stereochenol A (*1*)

Colorless gum; Electrospray MS: m/z $[M + H]^+$ 293.2, $C_{19}H_{16}O_3 + H$; ^1H NMR: δ 8.25 (2H, dd, $J = 7.5$, 1.5 Hz, H-3, H-6), 8.1(1H, d, $J = 7.8$ Hz, H-11), 7.77 (2H, br d, $J = 7.5$ Hz, H-4, H-5), 7.58(1H, d, $J = 8.1$ Hz, H-12), 3.10 (2H, t, $J = 7.5$ Hz, H_2-15), 2.79 (3H, s, H_3-18), 2.77 (2H, t, $J = 7.5$ Hz, H_2-14), 2.19 (3H, s, H_3-19).

3.5. Stereochenol B (*2*)

Pale yellow solid; Electrospray MS: m/z $[M + H]^+$ 325.2, $C_{20}H_{20}O_4 + H$; ^1H NMR: δ 8.10 (1H, dd, $J = 1.2$, 7.8 Hz, H-6), 7.90 (1H, $J = 1.2$, 7.2 Hz, H-3), 7.68 (1H, ddd, $J = 1.2$, 7.2, 7.8 Hz, H-4), 7.53 (1H, d, $J = 7.0$ Hz, H-11), 7.47 (1H, ddd, $J = 1.2$, 7.2, 7.8 Hz, H-5), 4.25 (1H, d, $J = 7.5$ Hz, H_a-20), 3.78 (1H, d, $J = 7.5$ Hz, H_b-20), 2.96 (1H, dd, $J = 4.2$, 7.0 Hz, H-12), 1.91–1.93 (2H, m, H-15), 1.85 (1H, m, H-16), 0.55 (3H, s, H_3-18), 1.58 (2H, m, H-14), 1.19 (3H, s, H_3-19).

3.6. Sterekunthal B (*3*)

Colorless gum; Electrospray MS: m/z $[M + H]^+$ 323.3, $C_{20}H_{18}O_4 + H$; ^1H NMR spectral data identical to those published previously.

3.7. Sterequinone C (*4*)

Colorless gum; Electrospray MS: m/z $[M + H]^+$ 293.2, $C_{19}H_{16}O_3 + H$; ^1H NMR spectral data identical to published values.

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