Studies on polynuclear furoquinones. Part 1: Synthesis of tri- and tetra-cyclic furoquinones simulating BCD/ABCD ring system of furoquinone diterpenoids

Faruk H. Shaik and Gandhi K. Kar*

Abstract

Synthesis of phenanthro[1,2-b]furan-10,11-dione, the core nucleus present in Tanshinone-I is described in 8–10 steps starting from 2-bromo-3,4-dihydro-1-naphthaldehyde. The bromoaldehyde was converted to methyl 2-(2-bromo-1-naphthyl)acetate or 2-(2-bromo-1-naphthyl)acetonitrile following the protocol of functional group transformations. Subsequent Suzuki coupling of this ester/nitrile derivative with furan-2-boronic acid produced [2-(2-furyl)-1-naphthyl]acetic ester/nitrile which on hydrolysis furnished the corresponding acid derivative. Cyclization of the acid followed by oxidation of the phenol, with Fremy’s salt, produced the tetracyclic furoquinone, phenanthro[1,2-b]furan-10,11-dione. This method has also been extended for the synthesis of the tricyclic furoquinone, naphtho[1,2-b]furan-4,5-dione.

Introduction

Chemistry of furoquinones [1-8], especially the tetra cyclic furoquinones isolated from Chinese red rooted sage *Salvia miltiorrhiza* Bunge known as “*Dan Shen*” in Chinese traditional medicine, attracted the attention of synthetic chemists as well as medicinal chemists due to the various biological activities displayed by such class of compounds. *Dan Shen* is used clinically for treatment of viral hepatitis, cardiac and vascular disorder, hypertension, miscarriage and menstrual disorder [3,9] etc. It has been reported to show potential anticancer activity [10] (against human breast cancer), cytotoxic and antiplatelet aggregation activities [1,11]. It also acts as an antibacterial [1], antioxidant and anti-inflammatory agent [12-14] as well as induces apoptosis in human leukemia cell lines [15,16]. It is believed that broad spectrum of activities of *Dan Shen* are mainly associated with the presence of tetra cyclic furoquinone diterpenoids like Tanshinone I [17,18], Tanshinone IIA and IIB [19-26], Cryptotanshinone [20,22], Nortanshinone [23,27], Tanshindiol [23,27] etc. (Figure 1). Even the tricyclic furoquinones (Figure 1) have also been reported to possess cancer chemo preventive activity [28].
Figure 2: Key strategies for development of C-ring with quinone functionality.

Retrosynthesis of the molecule showed that the required phenolic compound can easily be achieved in 7–8 steps starting from 2-bromo-3,4-dihydro-1-naphthaldehyde (a substrate easily available by Vilsmeier–Haack reaction on 2-tetralone) and furan-2-boronic acid (a commercially available material) (Figure 3).

Results and Discussion

Our aim is to develop a general route for the synthesis of tricyclic/tetracyclic furoquinones with structural diversity. Our approach is shown in Scheme 1 and Scheme 2. In the synthesis of the tetra cyclic furoquinone 13, an easily available starting material 2-bromo-3,4-dihydro-1-naphthaldehyde 1 [34] was utilized as A, B ring precursor and commercially available furan 2-boronic acid as D-ring precursor. In the event of the synthesis, the C ring was constructed to reach the target molecule in 8-10 steps. The key steps in our synthesis deal with the formation of aryl-furyl C–C bond via Suzuki reaction [35] and the generation of the quinone functionality by oxidation of a phenolic intermediate (Figure 2).

In all of these compounds the key structural unit present is a furophenanthraquinone or a furonaphthoquinone as well as their di/tetra/hexahydro analog.

We have not come across any synthesis of phenanthro[1,2-b]furo-10,11-dione (13) (the nuclear core structure of Tanshinone-I) though a number of syntheses of naturally occurring tetra cyclic furoquinone diterpenoids have been reported in literature [18-27] in the last few decades. In comparison only very few syntheses of tricyclic furoquinone 18 [29,30] and its derivatives [31-33] have been reported. Encouraged by the broad spectrum biological activity of furoquinones, we aimed to synthesize novel polynuclear furoquinones. Herein we report the synthesis of tetra cyclic furoquinones, phenanthro[1,2-b]furan-10,11-dione (13) and the tricyclic furoquinone, naphtho[1,2-b]furan-4,5-dione (18), simulating respectively the A-B-C-D/B-C-D ring of Tanshinone-I, through a novel pathway.

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Scheme 1: Reagents and conditions: i) DDQ (1.5 equiv), dry benzene, reflux, argon atmosphere, 37 h, 83%. ii) NaBH₄, EtOH, room temperature, 2 h, 94%. iii) PBr₃, CCl₄, 60 °C, 1 h, 92%. iv) KCN, DMF, room temperature, overnight then 1 h at 50 °C, 68%. v) KOH, EtOH, H₂O, reflux, 23 h, 74%. vi) CH₃NH₂, ether, 0 °C-room temperature, 95%. vii) furan-2-boronic acid (1.2 equiv.), Et₃N, DMF, Pd(PPh₃)₄ (2 mol %), 110 °C, argon atmosphere, 53 h, 77%. viii) KOH (2 equiv), EtOH, H₂O, reflux, 15 h, 85%. ix) furan-2-boronic acid (1.2 equiv), Et₃N, DMF, Pd(PPh₃)₄ (2 mol %), 110 °C, argon atmosphere, 37 h, 66%. x) KOH, EtOH, H₂O, reflux, 45 h, 48%. xi) TFAA, TFA, room temperature, overnight, 71%, xii) Fremy’s salt (3 equiv), MeOH, 1/6 M Na₂HPO₄ solution. 0–5 °C, overnight, 48%. (All yields are for purified products only.)

When 2-bromo-3,4-dihydro-1-naphthaldehyde (easily obtained in 68% yield by the reaction of 2-tetralone and PBr₃/DMF in CHCl₃ at room temperature) was aromatized with DDQ in refluxing benzene, 2-bromo-1-naphthaldehyde (2) was produced in excellent yield. Reduction (NaBH₄/EtOH) of the aldehyde 2 produced the alcohol 3 as a colorless solid, in 94% yield, which on reaction with PBr₃/CCl₄ produced the bromide 4 as a light yellow solid. The bromide was then converted (KCN/DMF) to the nitrile derivative 5 which on hydrolysis (KOH/EtOH-H₂O, reflux) followed by esterification with CH₃NH₂ furnished methyl 2-(2-bromo-1-naphthyl)acetate 7 in overall good yield. The bromo ester was then subjected to Suzuki reaction with furan-2-boronic acid.

Reaction of compound 7 with furan-2-boronic acid in the presence of Et₃N and Pd(PPh₃)₄ (cat.) in DMF under argon atmo-

Scheme 2: Reagents and conditions: i) furan-2-boronic acid (1.2 equiv), Et₃N, DMF, Pd(PPh₃)₄ (2 mol %), 110 °C, N₂ atmosphere, 7 h, 84%. ii) KOH, EtOH, H₂O, reflux, 9 h, 90%. iii) TFAA, TFA, room temperature, overnight, 54%. iv) Fremy’s salt (~2.5 equiv), MeOH, 1/6 M Na₂HPO₄ solution, 0–5 °C, overnight, 56%. (All yields are for purified products only.)
sphere produced methyl [2-(2-furyl)-1-naphthyl]acetate 8 (77%) which when hydrolyzed furnished [2-(2-furyl)-1-naphthyl]acetic acid (9) in 85% yield. The acid 9 was also synthesized via hydrolysis of the nitrile derivative 10 which in turn was obtained in 66% yield, by direct Suzuki reaction of 5 with furan-2-boronic acid. However in this case as the intermediate amide 11 produced was resistant to further hydrolysis, the reaction required prolonged reflux and also the yield was relatively poor. Even after reflux of the nitrile derivative 10 in KOH/EtOH-H$_2$O for 45 h 20% of the amide 11 was recovered along with 48% of the desired carboxylic acid. Change of solvent and conditions (e.g., replacement of ethanol with other high boiling alcohols or use of THF as co-solvent and higher temperature) produced no better result. The next step was the introduction of the phenol functionality. In this case our early attempt to prepare the phenol 12 by PPA cyclization of the acid 9 was unsuccessful. We however successfully prepared the phenol as a light yellow solid by cyclization of the acid 9 with trifluoroacetic acid (TFA) and trifluoroacetic anhydride (TFAA) at room temperature in 71% yield. The phenol 12 was finally oxidized (with Fremy’s salt) [36-38] to the o-quinone 13 to complete the synthesis of phenanthro[1,2-b]furan-10,11-dione. The compounds were characterized by usual spectroscopic and analytical methods ($^1$H NMR, $^{13}$C NMR, IR, HRMS etc.).

The developed pathway was then applied for the synthesis of tricyclic furoquinone 18 (naphtho[1,2-b]furan-4,5-dione) starting from methyl (2-bromophenyl)acetate 14 and furan-2-boronic acid (Scheme 2).

When methyl (2-bromophenyl)acetate 14 was subjected to Suzuki reaction with furan-2-boronic acid, produced [2-(2-furyl)phenyl]acetic ester 15 as a pale yellow liquid in 84% yield. Subsequent alkaline hydrolysis of 15 produced the carboxylic acid 16 as a white solid in 90% yield. Synthesis of the furonaphthol 17 was achieved in good yield, by cyclization of the carboxylic acid 16 with TFA and TFAA at room temperature. Finally oxidation of the naphthol derivative 17, with Fremy’s Salt, resulted in the formation of naphtho[1,2-b]furan-4,5-dione (18), as a red solid, in 56% yield. The compounds have been characterized by usual spectroscopic analysis (NMR, IR and HRMS data) as well as by analogy with literature report [30].

In general we have developed a novel pathway for the synthesis of polynuclear furoquinones simulating BCD/ABCD ring of natural furoquinone (Tanshinone-I) and we believe the method has great potential towards the synthesis of various polynuclear furoquinone derivatives bearing electron donating/electron withdrawing functionality within its framework as bromoaldehyde derivatives bearing such groups can easily be obtained from corresponding ketones by Vilsmeier–Haack reaction. Very recently we have reported a general method for the synthesis of $\beta$-(2-furyl)-$\alpha,\beta$-unsaturated aldehydes [39] via Suzuki reaction of $\beta$-bromo-$\alpha,\beta$-unsaturated aldehydes. These substrates can be used for the synthesis of various non-natural tricyclic and “U-shaped” tetra cyclic furoquinone derivatives. The work is under progress and the results will be published in due course.

**Experimental**

Furan-2-boronic acid, 2-tetralone and tetrakis(triphenylphosphine)palladium(0) and DDQ were purchased from Sigma-Aldrich (U.S.A). Trifluoroacetic anhydride was purchased from Alfa Aesar (Lancaster). 2-Bromo-3,4-dihydronaphthalene-1-carbaldehyde was prepared from 2-tetralone by Vilsmeier–Haack reaction. Solvents were dried following standard literature procedure. Fremy’s salt (potassium nitrosodisulfonate) was prepared in the laboratory as per literature procedure [36].

![Figure 4: Assignment of chemical shifts ($^1$H NMR and $^{13}$C NMR) of compound 13.](image-url)
1H NMR spectra were recorded on Bruker 500 MHz (at Chemgen Pharma, Kolkata) and Bruker 400 MHz (at Chembiotech International, Kolkata) and Bruker 300 MHz (IACS, Kolkata) NMR spectrometer respectively. ESI mass spectra were recorded on a micro mass Q-TOF mass spectrometer (serial no. YA 263) at IACS, Kolkata. IR spectral data were obtained from a JASCO FT/IR680 PLUS Spectrometer.

[2-(Furan-2-yl)-naphthalen-1-yl]acetic acid methyl ester (8)
A mixture of compound 7 (150 mg, 0.54 mmol), furan-2-boronic acid (75 mg, 0.64 mmol) and Et3N (0.5 mL, 3.6 mmol) was degasified with argon for 25 minutes. Now to it the catalyst Pd(PPh3)4 (~15 mg, 2 mol %) was added. The mixture was then heated with stirring under argon at 110 °C till the reaction was completed (~53 h). After cooling to room temperature, the mixture was poured into cold water and extracted with ether. Organic layer was washed successively with NaHCO3 solution, 5% brine and dried (Na2SO4) and solvent removed. Crude product thus obtained was then purified by column chromatography [silica gel/pet. ether (60–80 °C) and ethyl acetate mixture, 10:1]. Compound 8 was obtained as a white solid (110 mg) in 77% yield, m.p., 109–111 °C. IR(KBr) νmax : 1737.6 cm−1; 1H NMR (400 MHz, CDCl3) δ: 3.72 (3H, s), 4.33 (2H, s), 6.63 (1H, t, J = 7.1 Hz), 6.68 (1H, d, J = 3 Hz), 7.70 (1H, t, J = 7.2 Hz), 7.56 (1H, d, J = 7.2 Hz), 7.57 (1H, br s), 7.72 (1H, d, J = 8.6 Hz), 7.82 (1H, d, J = 9.4 Hz), 7.84 (1H, d, J = 9.3 Hz), 8.01 (1H, d, J = 8.4 Hz), ppm.

[2-(Furan-2-yl)-naphthalen-1-yl]acetic acid (9)
A mixture of compound 8 (100 mg, 0.38 mmol), KOH (43 mg, 0.76 mmol), 2 mL water and 2 mL ethanol was refluxed on a water bath for 15 h. Excess EtOH was distilled out as much as possible and then the residue was diluted with 2–3 mL of water. Neutral part was extracted with ether. Aqueous alkaline part was cooled in ice and acidified with HCl. Separated solid was thoroughly extracted with ethyl acetate. After usual work up, 80 mg (85%) of the acid 9 was obtained as white solid, m.p., 197–199 °C. IR (KBr) νmax 1692.2 cm−1. (Treatment of the acid 9 with diazomethane in ether produced the methyl ester derivative identical with compound 8.)

Phenan thro[1,2-b]furan-11-ol (12)
A mixture of compound 9 (100 mg, 0.39 mmol), 3 mL trifluoroacetic acid, 0.9 mL trifluoroacetic acid was stirred at room temperature overnight protecting from moisture. The mixture was then poured in ice cold saturated NaHCO3 solution and stirred well and extracted thoroughly with CH2Cl2. The organic layer was washed with aq. NaHCO3 solution and finally with H2O and dried (Na2SO4). Removal of solvent afforded the crude product which was purified by column chromatography [silica gel/pet. ether (60–80 °C) and ethyl acetate mixture, 19:1] to furnish 65 mg (71%) of 12 as a light yellow solid, m.p., 175–177 °C. IR (KBr) νmax 3225, 3302 cm−1; 1H NMR (500 MHz, CDCl3) δ: 5.47 (1H, s), 7.04 (1H, br s), 7.58 (1H, t, J = 7.4 Hz), 7.63 (1H, t, J = 7.5 Hz), 7.75 (1H, d, J = 8.8 Hz), 7.78 (1H, br s), 7.85 (1H, s), 7.91 (1H, d, J = 7.8 Hz), 8.22 (1H, d, J = 8.8 Hz), 8.55 (1H, d, J = 8.2 Hz) ppm.

Phenan thro[1,2-b]furan-10,11-dione (13)
To a stirred solution of potassium nitrosodisulfonate (Fremy’s salt) (170 mg, 0.65 mmol) in 12 mL 1/6 (M) Na2HPO4 solution taken in a 50 mL round bottomed flask, a solution of the furanophthalid derivative 12 (50 mg, 0.21 mmol) in 6 mL methanol was added drop wise. Stirring was continued at 0–5 °C for 2 h and then left overnight in freezer. The dark red solid separated was filtered and purified by column chromatography [silica gel/ pet. ether (60–80 °C) and ethyl acetate, 10:1]. An analytical sample was prepared further by recrystallisation from pet ether–ethyl acetate mixture. Yield, 25 mg (48%), m.p., 178–180 °C. IR (KBr) νmax 1686, 1667 cm−1; 1H NMR (500 MHz, CDCl3) δ: 6.87 (1H, br s), 7.53 (1H, d, J = 7.5 Hz), 7.55 (1H, br s), 7.70 (1H, br t, J = 7.5 Hz), 7.81–7.85 (2H, a doublet and a triplet merged together), 8.12 (1H, d, J = 8.5 Hz), 9.40 (1H, d, J = 8.5 Hz) ppm; 13C NMR (125 MHz, CDCl3) δ: 109.11, 119.16, 120.79, 122.88, 126.66, 127.66, 129.20, 130.07, 131.20, 132.47, 134.65, 137.33, 145.54, 161.31, 174.53, 183.07 ppm; HRMS (ESI, 70 eV): m/z = 271.0372 [M+Na] (calculated mass for C17H12O3Na: 271.0371 [M+Na]).

Naphtho[1,2-b]furan-4,5-dione (18)
To a stirred solution of potassium nitrosodisulfonate (Fremy’s salt) (170 mg, 0.63 mmol) in 5 mL 1/6 (M) Na2HPO4 solution taken in a 25 mL round bottomed flask, a solution of the furanophthalid derivative 17 (50 mg, 0.27 mmol) in 2 mL methanol was added drop wise. Stirring was continued at 0–5 °C for 2 h and then left overnight in freeze. The brick red solid separated was filtered to obtain 35 mg of crude product which on purification by column chromatography (silica gel/pet. ether–ethyl acetate, 5:1) afforded 30 mg (56%) of the title compound (18). An analytical sample was prepared by further recrystallisation from pet. ether–EtOAc mixture; m.p., 205–206 °C (lit. [30] m.p. 217–218 °C). IR(KBr) νmax 1785 cm−1; 1H NMR (500 MHz, CDCl3) δ: 6.88 (1H, d, J = 1.8 Hz), 7.48 (1H, t, J = 7.5 Hz), 7.51 (1H, d, J = 1.8 Hz), 7.67 (1H, t, J = 7.5 Hz), 7.74 (1H, d, J = 7.5 Hz), 8.1 (1H, d, J = 7.7 Hz) ppm; 13C NMR (125 MHz, CDCl3) δ: 108.94, 121.56, 122.41, 128.49, 128.81, 130.36, 130.64, 135.48, 145.13, 160.64, 174.54, 180.56 ppm. HRMS (ESI, 70 eV): m/z = 199.0399 [M+H] (calculated mass for C12H10O3: 199.0391 [M+H]+), 1H NMR (300 MHz, CDCl3) δ: 8.09 (1H, d, J = 7.9 Hz), 7.73–7.62 (2H, m), 7.49 (1H, d, J = 2.0 Hz), 7.45 (1H, m), 6.86 (1H, d, J = 2.0 Hz).
Supporting Information

Supporting information features experimental procedures, analytical data and NMR spectra for some selected compounds.

Supporting Information File 1

Experimental procedures
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-5-47-S1.doc]

Supporting Information File 2

$^1$H and $^{13}$C NMR Spectra.
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Acknowledgments

Financial support [project no. 01(1976)/05/EMR-II] from CSIR, New Delhi is gratefully acknowledged. We are also thankful to CSIR for providing a NET fellowship to one of the author (FHS).

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