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Syntheses of Arnottin I and Arnottin II

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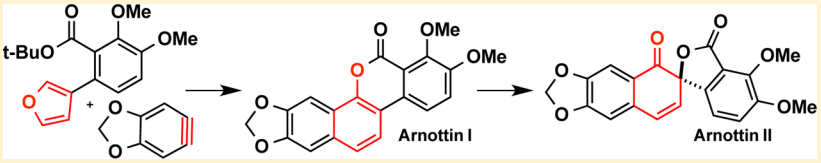
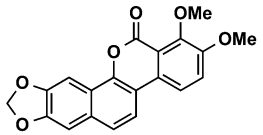
Supporting Information

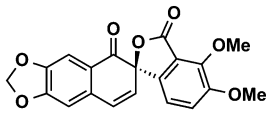


ABSTRACT: Short total syntheses of arnottin I and II were accomplished in 5 and 6 steps, respectively. A sesamol-benzyne cycloaddition with a 3-furyl-benzoate followed by regiospecific lactonization provided rapid, large-scale access to the core of arnottin I. Saponification of arnottin I and hypervalent iodide mediated spirocyclization provided an efficient and direct preparation of racemic arnottin II.

The arnottins (I and II) are coumarin-type natural products isolated from the bark of the *Xanthoxylum arnottianum Maxim* (rutaceae) and are surmised to possess antibiotic properties.[1] Syntheses of these interesting metabolites have been reported after the initial isolation and structural determination.[2] The absolute stereochemical configuration of spirocyclic arnottin II was synthetically determined via asymmetric dihydroxylation of a reduced isomer of arnottin I by Yamaguchi and co-workers.[2c]



Arnottin I (1)

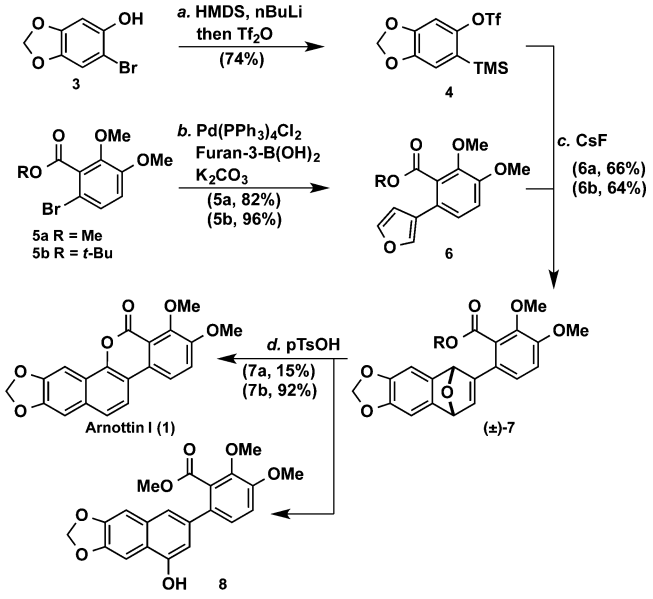


Arnottin II (2)

Tandem oxidative dearomatization and spirocyclization[3] is capable of converting simple benzocoumarins to chiral spirocyclic lactones that are found in several natural product families. The direct conversion of arnottin I to arnottin II using this method has not yet been reported. Hypervalent iodide mediated oxidative dearomatization has been employed in the synthesis of various natural products including galanthamine and other *amaryllidaceae* alkaloids.[4,5] Recent advances have allowed for asymmetric hypervalent iodide oxidative dearomatization;[6,7] however, few examples exist within total synthesis. To study and expand upon current methods for hypervalent iodide mediated spirocyclization, a short and concise synthesis of the arnottins was pursued. The preparation of arnottin I utilized a benzyne cycloaddition, hydrolysis, and oxidative spirocyclization to arnottin II to provide large quantities of the metabolites for testing.

A convergent synthetic path to arnottin I was planned using a benzyne cycloaddition with a 3-furyl benzoate, followed by lactone formation (Scheme 1). Bis-lithiation of 6-bromosesamol,[8] followed by trimethylsilyl chloride quench and triflation using under Mori's procedure[9] afforded benzyne precursor **4** in 74% overall yield on 5 g scale. The furyl coupling partner was

Scheme 1. Preparation of Arnottin I



prepared from readily available dimethoxybenzoic acid and converted to either the methyl (**5a**) or *tert*-butyl bromoester (**5b**) in 2 steps.[2c] The bromoester (**5**) was cross-coupled under Suzuki's condition with commercially available 3-furylboronic acid in 82 and 96% yield for the methyl and *tert*-butyl ester, respectively. The benzyne-mediated cycloaddition proved capricious and required the sesamol silyltriflate to be used in excess (1.4 equiv) with slow generation of the benzyne using weakly soluble CsF in acetonitrile. The *in situ* cycloaddition produced the arnottin I progenitors (rac-**7a**, rac-**7b**) in 66 and 64% yield, respectively.

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Unsaturated bicyclic ethers, such as **7**, can be converted to naphthols under a variety of conditions including Bronsted acids,[10] ruthenium,[11] rhodium,[12] and aluminum complexes.[13] The naphthol regioisomer produced is less predictable and was unknown for structure **7** at the onset of these studies. For the transformation of esters rac-**7a** and rac-**7b** to **1**, several conditions were attempted: Lewis acids such as BF_3-etherate or $Sc(OTf)_3$ gave complex mixtures and nucleophiles such as NaI and NaBr resulted in degradation. Bronsted acids were most effectual with HCl and TsOH both providing arnottin I for rac-**7a** and rac-**7b** in differing yield. Exposure of methyl ester rac-**7a** to TsOH in methanol led to nonregiospecific naphthol formation resulting in both arnottin I (15%) and the 4-naphthol derivative **8**.[14] Identical reaction conditions were attempted with *tert*-butyl ester rac-**7b** and surprisingly led to clean conversion of arnottin I in 92% yield with no 4-naphthol derivative observed. The synthetically prepared arnottin I displayed spectroscopic and physical properties identical to the natural product.[1] The disparity in reaction yield between rac-**7a** and rac-**7b** to arnottin I and the absent 4-naphthol derivative in the rac-**7b** reaction suggests the mechanism follows different paths for each ester employed. The methyl ester (rac-**7a**) produced both arnottin I and the 4-naphthol derivative suggesting naphthol formation occurred with little regiospecificity. The resultant 1-naphthol produced arnottin I whereas the 4-naphthol was incapable of cyclization. The *tert*-butyl ester (rac-**7b**) cleanly afforded arnottin I, suggesting the ester is deprotected prior to naphthol formation. One plausible mechanism is the weakening of a *tert*-butyl ester proton due to carbonyl lone-pair donation into the C−O σ^* of the bicycle, resulting in loss of isobutylene and carboxylate promoted rupture of the allylic ether as shown by intermediate **9** (Figure 1). The resultant benzylic alcohol (**10**) is quickly dehydrated to

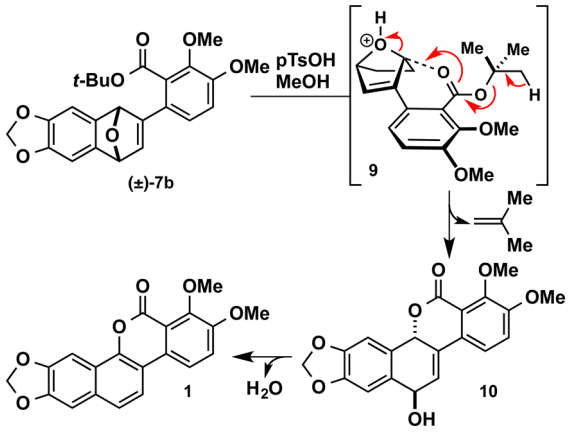


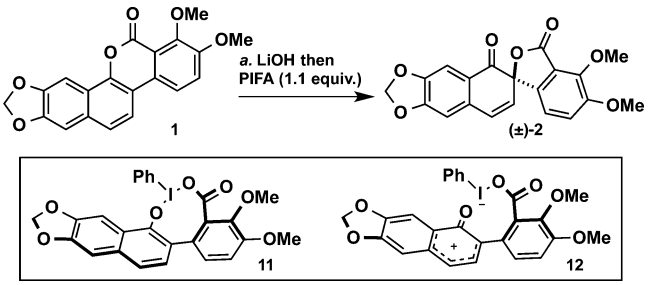
Figure 1. Proposed carboxylate-assisted lactonization cascade.

arnottin I. Furthermore, *in situ* ^{1}H NMR, showed no *tert*-butanol formation during the course of the reaction discouraging the phenol formation and lactonization scenario. Isobutylene was not observed; however, volatility would make detection difficult. The fortuitous sequence afforded large quantities of arnottin I and allowed the study of conversion to arnottin II.

Saponification of arnottin I required immediate exposure to spirocyclization conditions due to competitive recyclization and recovery of arnottin I in acid. Careful hydrolysis of arnottin I was followed by protonation of the carboxylate to a pH of 2−3, which reduced the conversion to arnottin I and retained solubility for the spirocyclization studies.

The saponified phenol acid was immediately exposed to different hypervalent iodide conditions to effect the spirocyclization. The highly reactive bis(trifluoroacetoxy)iodobenzene (PIFA) was necessary to form racemic arnottin II in DCM with cesium carbonate as an additive in 23% yield (Table 1, entry 1).

Table 1. Screen of hypervalent iodide conditions



entry	solvent	additive	time (h)	temp (°C)	yield (%)[a]
1	DCM	$CsCO_3$	4	−40	23
2	TFE		4	−20	25
3	HFIP		12	0	40
4	DCM/HFIP		12	0	28
5	HFIP	Et_3N, DMAP	12	0	35
6[b]	HFIP/MeCN	$MgClO_4$	12	0	25
7[b]	HFIP		12	0	56

[a]Yield refers to isolated yields following silica gel chromatography. [b]Syringe pump addition of PIFA over 1 h.

Kita noted substantial increases in yield using fluorinated solvents[10] that were also investigated. Trifluoroethanol (TFE, entry 2, 25%) was inferior as compared to hexafluoroisopropanol (HFIP, entry 3, 40%) as solvent. Blends of DCM and HFIP (entry 4, 28%) did not offer enhanced yields. An intensely colored intermediate was formed over the first 20 min of the reaction and persisted throughout the duration of the reaction. Two possible intermediates could exist; a ligand exchanged trapped γ^3-iodane **11**, or a dissociated cationic complex **12**.[4b] We reasoned the breakdown of the mixed hypervalent intermediate could occur through liberation of the weaker carboxylate donor using a nucleophilic donor. DMAP (entry 5) was added to the reaction, but did not increase the yield substantially as compared to its absence (entry 3). Perchlorate salts, known to increase yields involving nucleophilic addition to phenoxenium radical cations,[15] also did not improve the reaction and had noted degradation (entry 6). Slow addition of PIFA over 1 h provided a boost in yield and generated arnottin II in 56% overall yield over the two steps (entry 7). Attempts at asymmetric spirocyclization using chiral hypervalent iodide sources are planned.

In conclusion, we developed an efficient route from readily available materials to the arnottins using a benzyne cycloaddition and regiospecific ether fragmentation−lactonization cascade. Several other coumarin based natural products can now be accessed more efficiently using this tactic.

EXPERIMENTAL SECTION

***tert*-Butyl 6-(Furan-3-yl)-2,3-dimethoxybenzoate (6b).** A total of 1.43 g (4.50 mmol, 1.0 equiv) of *tert*-butyl 6-bromo-2,3-dimethoxybenzoate (**5b**),[2c] 750.0 mg (6.76 mmol, 1.5 equiv) of furan-3-boronic acid, and 1.865 g (13.50 mmol, 3.0 equiv) of K_2CO_3

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were dissolved in DMF (30.0 mL). The resulting solution was degassed under argon for 10 min. Then, 253.0 mg of $Pd(PPh_3)_2Cl_2$ (1.06 mmol, 8 mol %) and H_2O (10.0 mL) were added to the reaction flask, and this solution was stirred at 90 °C for 4 h. The reaction mixture was run through a Celite plug, diluted with toluene (10.0 mL), and concentrated *en vacuo*. This product was purified by column chromatography (3:1 hexanes/EtOAc, v/v) and dried under vacuum to yield 1.32 g of *tert*-butyl 6-(furan-3-yl)-2,3-dimethoxybenzoate (**6b**, 96% yield) as a white solid. Mp 46−48 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, J = 1.6, 0.9 Hz, 1H), 7.42 (t, J = 1.7 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 6.92 (d, J = 8.5 Hz, 1H), 6.56 (dd, J = 1.8, 0.9 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 151.8, 145.8, 142.8*, 142.7*, 139.7*, 139.6*, 130.4, 124.8, 123.7, 122.5, 113.1, 111.2*, 111.1*, 82.3, 61.5, 56.0, 28.1 (*denotes rotamers); IR (neat, cm^{-1}) 2973, 2935, 1715, 1482, 1291, 1265, 1059, 1029, 795; TLC R_f = 0.60 (3:1 hexanes/EtOAc, v/v); HRMS (DART) m/z calcd for $C_{17}H_{21}O_5$ $(M + H)^+$: 305.1389, found 305.1375.

Methyl 6-(Furan-3-yl)-2,3-dimethoxybenzoate (6a). A total of 2.00 g (18.0 mmol) of methyl 6-bromo-2,3-dimethoxybenzoate (**5a**) yielded 3.53 g (12.5 mmol, 82% yield) of methyl 6-(furan-3-yl)-2,3-dimethoxybenzoate (**6a**) according to the above procedure. Mp 43−45 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, J = 1.6, 0.9 Hz, 1H), 7.42 (t, J = 1.7 Hz, 1H), 7.10 (d, J = 8.5 Hz, 1H), 6.96 (d, J = 8.5 Hz, 1H), 6.50 (dd, J = 1.8, 0.9 Hz, 1H), 3.89 (s, 3H), 3.89 (s, 3H), 3.83 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.3, 151.6, 145.9, 143.0, 139.1, 128.3, 124.5, 123.8, 122.6, 113.6, 110.3, 61.5, 55.8, 52.3; IR (neat, cm^{-1}) 2950, 1723, 1500, 1258, 905, 804; TLC R_f = 0.40 (2:1 hexanes/EtOAc, v/v); HRMS (DART) m/z calcd for $C_{14}H_{14}O_5$ $(M + H)^+$: 262.0841, found 262.0838

***tert*-Butyl 6-(5,8-Dihydro-5,8-epoxynaphtho[2,3-*d*][1,3]-dioxol-6-yl)-2,3-dimethoxybenzoate (7b).** A total of 335.0 mg (1.036 mmol, 1.4 equiv) of 6-(trimethylsilyl)benzo[*d*][1,3]dioxol-5-yl-trifluoromethanesulfonate (**4**)[9] and 225.0 mg (0.74 mmol, 1.0 equiv) of *tert*-butyl 6-(furan-3-yl)-2,3-dimethoxybenzoate (**6b**) were dissolved with acetonitrile (10.0 mL) in a flame-dried flask. The solution was charged with argon; then 337.0 mg (2.22 mmol, 3.0 equiv) of CsF was added, and the reaction mixture was let to stir at 23 °C for 24 h. The solution was diluted with water (30.0 mL) and extracted with ethyl acetate (3 × 15.0 mL). The combined organic layers were washed with water (30.0 mL) and brine (30.0 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The product was purified by column chromatography (3:1 hexanes/EtOAc, v/v) to yield 201.6 mg of *tert*-butyl 6-(5,8-dihydro-5,8-epoxynaphtho[2,3-*d*][1,3]dioxol-6-yl)-2,3-dimethoxybenzoate (**7b**, 64% yield) as an off-white solid. Mp 150 °C (decomp.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, J = 8.5 Hz, 1H), 6.94 (m, 2H), 6.89 (d, J = 8.6 Hz, 1H), 6.83 (t, J = 0.5 Hz, 1H), 5.94 (d, J = 1.4 Hz, 1H), 5.86 (d, J = 1.4 Hz, 1H), 5.79 (t, J = 0.8 Hz, 1H), 5.73 (dt, J = 1.8, 0.8 Hz, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.7, 153.3, 152.6, 146.2, 144.8, 144.4, 143.4, 143.0, 136.7, 129.7, 122.9, 122.1, 112.6, 104.0, 103.7, 101.3, 85.0, 84.0, 82.4, 61.5, 56.1, 28.1; IR (neat, cm^{-1}) 2973, 2935, 1715, 1482, 1292, 1265, 1142, 1059, 1029, 795; TLC R_f = 0.31 (3:1 hexanes/EtOAc, v/v); HRMS (DART) m/z calcd for $C_{20}H_{17}O_7$ $(M - C_4H_8)^+$: 369.0974, found 369.0960.

Methyl 6-(5,8-Dihydro-5,8-epoxynaphtho[2,3-*d*][1,3]dioxol-6-yl)-2,3-dimethoxybenzoate (7a). A total of 780.0 mg (2.23 mmol) of methyl 6-(furan-3-yl)-2,3-dimethoxybenzoate (**6a**) yielded 375.0 mg (0.98 mmol, 66% yield) of methyl 6-(5,8-dihydro-5,8-epoxynaphtho[2,3-*d*][1,3]dioxol-6-yl)-2,3-dimethoxybenzoate (**7a**) as per the above procedure. Mp 56−58 °C (decomp); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.98 (d, J = 8.6 Hz, 1H), 6.93 (m, 2H), 6.81 (m, 2H), 5.93 (d, J = 1.4 Hz, 1H), 5.87 (d, J = 1.4 Hz, 1H), 5.75 (t, J = 0.8 Hz, 1H), 5.71 (dt, J = 1.8, 0.8 Hz, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.77 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 153.5, 152.4, 146.3, 144.7, 144.3, 143.1, 142.6, 136.5, 127.6, 123.4, 122.0, 113.1, 103.9, 103.5, 101.2, 84.9, 83.9, 61.6, 56.0, 52.5; IR (neat, cm^{-1}) 2941, 1724, 1460, 1254, 1035; TLC R_f = 0.5 (2:1 hexanes/EtOAc v/v); HRMS (DART) m/z calcd for $C_{21}H_{19}O_7$ $(M + H)^+$: 383.1131, found 383.1129.

Arnottin I (1). A total of 150.0 mg (0.354 mmol, 1.0 equiv) of *tert*-butyl 6-(5,8-dihydro-5,8-epoxynaphtho[2,3-*d*][1,3]dioxol-6-yl)-2,3-dimethoxybenzoate (**7b**) was added to a flame-dried round-bottomed flask and dissolved in anhydrous MeOH (5 mL). Next 15.2 mg (0.0884 mmol, 0.25 equiv) of *p*-toluenesulfonic acid was added to this solution and the mixture stirred at 50 °C under nitrogen atmosphere for 24 h. The reaction mixture was then cooled to 0 °C and filtered, and the off-white solid was washed with cold MeOH. This product was dried under vacuum to yield 113.4 mg of arnottin I (**1**, 92% yield). Mp >250 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 8.9 Hz, 1H), 7.85 (s, 1H), 7.84 (d, J = 8.8 Hz, 1H), 7.54 (d, J = 8.8 Hz, 1H), 7.45 (d, J = 8.8 Hz, 1H), 7.14 (s, 1H), 6.10 (s, 2H), 4.03 (s, 3H), 3.99 (s, 3H); ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.08 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 8.7 Hz, 1H), 7.66 (app t, J = 9.4 Hz, 2H), 7.59 (s, 1H), 7.34 (s, 1H), 6.17 (s, 2H), 3.97 (s, 3H), 3.92 (s, 3H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 155.7, 152.5, 150.8, 148.0, 147.9, 144.8, 130.5, 128.7, 122.5, 120.8, 118.8, 117.7, 117.7, 114.1, 111.5, 103.5, 101.0, 96.9, 60.2, 56.3; IR (neat, cm^{-1}) 3010, 2943, 1734, 1489, 1463, 1276, 1122, 1039, 821; TLC R_f = 0.50 (1:1 hexanes/EtOAc, v/v); HRMS (DART) m/z calcd for $C_{20}H_{15}O_6$ $(M + H)^+$: 351.0869, found 351.0855.

Arnottin II (2). Arnottin I (**1**, 12.0 mg, 0.035 mmol) was suspended in 0.5 mL of THF:MeOH:H_2O (3:1:1, v/v/v) and 7.0 mg (0.17 mmol, 5.0 equiv) of LiOH·H_2O was added. The reaction was heated at 50 °C for 2 h over which time the solution became red. The flask was cooled to 0 °C and 1 M HCl was added dropwise until the solution turned yellow-orange indicating a pH of 2−3. The solution was extracted with Et_2O (2 × 1.0 mL), dried over Na_2SO_4 and concentrated at 23 °C yielding an unstable yellow-orange solid. The flask was cooled to 0 °C and HFIP (0.50 mL) was added. PIFA (17.0 mg, 0.041 mmol, 1.1 equiv) in 0.50 mL of HFIP was added over 1 h at 0 °C via syringe pump and then the reaction was stirred at 23 °C. After 12 h the reaction was quenched with 1 M HCl (1.0 mL), extracted with CH_2Cl_2 (2 × 1.0 mL), dried over Na_2SO_4 and concentrated. Flash chromatography (2:1 hexanes/EtOAc, v/v) yielded arnottin II (**2**, 7.0 mg, 0.02 mmol, 56% yield) as an off yellow solid. Mp 206−208 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.05 (d, J = 8.3 Hz, 1H), 6.78 (m, 2H), 6.68 (d, J = 9.9 Hz, 1H), 6.09 (m, 4H), 4.17 (d, J = 0.8 Hz, 3H), 3.86 (s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 191.1, 167.6, 154.1, 153.6, 149.1, 148.6, 139.2, 134.6, 130.3, 128.4, 123.2, 119.2, 117.4, 115.6, 108.1, 107.7, 102.6, 84.5, 62.8, 57.0; IR (neat, cm^{-1}) 1682, 1770, 2853, 2921; TLC R_f = 0.45 (1:1 hexanes/EtOAc v/v); HRMS (DART) m/z calcd for $C_{20}H_{15}O_7$ $(M + H)^+$: 367.0818, found 367.0811.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H and ^{13}C NMR spectra for all new compounds is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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