Expedient syntheses of naturally occurring (±)-3-benzylphthalides and (±)-3-aryl-8-hydroxy-3,4-dihydroisocoumarins: Structure revision of the (±)-3-benzylphthalide isolated from *Frullania falciloba*

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A simple synthesis of (±)-3-benzyl-7-methoxyphthalides (**1b**, **1d** and **4a**–**c**) from 7-methoxyphthalides (**3a**–**c**) and a novel $AlCl_3$-catalysed conversion of (±)-3-benzyl-7-methoxyphthalides (**1d**, **4a**–**c**) to 4′-*O*-methylhydrangenol **5a**, 4′,6-*O,O*-dimethylthunberginol-C **5b** and related compounds (**5c** and **5d**) is described.

Introduction

Several 3-benzyl-7-hydroxy/methoxyphthalides and 3-aryl-8-hydroxy-3,4-dihydroisocoumarins have been isolated from natural sources. Thus, balantiolide **1a**, *O*-methylbalantiolide **1b** and the benzylphthalide **1c** have been isolated[1] from *Frullania muscicola*. The first isolation[2] of **1a** was reported in 1986 from the New Zealand liverwort *Balantiopsis rosea*. The phthalide **1d**, isolated[3] in 1987 from the Australian liverwort *Frullania falciloba*, was assigned structure **1e** on the basis of ^{1}H NMR spectral data. The revised structure **1d** has now been assigned to it.[4]

A large number of 3-aryl-8-hydroxy-3,4-dihydroisocoumarins, such as hydrangenol **2a**, phyllodulcin **2b** and thunberginols C, D, E and G **2c**–**f**, have been reported[5] from *Hydrangeae Dalcis folium* (Amacha in Japanese), the fermented and dried leaves of *Hydrangea macrophylla*. The leaves of this plant are used as a sweetening agent. Phyllodulcin **2b** shows antifungal activity and is found to be 600–800 times sweeter than sucrose.[6] The thunberginols[6] **2c**–**f** and hydrangenol 4′-*O*-glucoside[7] showed antiallergic activity in an *in vitro* bioassay using the Schults–Dale reaction in sensitized guinea pig bronchial muscle. These isocoumarins also exhibit antimicrobial[5,8] activity against oral bacteria.

In view of their natural occurrence, biological activities, and utility as synthetic intermediates, several methods have been developed for the synthesis of 3-benzylphthalides and 3-aryl-8-hydroxy-3,4-dihydroisocoumarins. Most of the methods reported[9] for the synthesis of 3-benzylphthalides involve formation of 3-benzylidenephthalides, which on catalytic hydrogenation provide the corresponding 3-benzylphthalides. The approaches developed[10] for 3-aryl-8-hydroxy-3,4-dihydroisocoumarins involve heteroatom-directed lithiation reaction of benzamides or cyclization of stilbenecarboxylic acids. The stilbenecarboxylic acids are obtained from 3-benzylphthalides or from phthalaldehydic acids and 2-halomethyl benzoates using the Wittig reaction. Most of the approaches for 3-benzylphthalides and 3-aryl-8-hydroxy-3,4-dihydroisocoumarins involve multistep sequences of reactions. The conversion of 3-benzylphthalides into 3-aryl-8-hydroxy-3,4-dihydroisocoumarins involves three steps.[10a] Hence, it was felt necessary to develop convenient methods for the synthesis of (±)-7-methoxy-3-benzylphthalides and (±)-3-aryl-8-hydroxy-3,4-dihydroisocoumarins.

Results and discussion

In continuation of our work on the synthesis of naturally occurring phthalides[9a] and 3-aryl-3,4-dihydroisocoumarins,[10h] we report herein a novel method for the synthesis of (±)-3-benzyl-7-methoxyphthalides (**1b**, **1d**, **4a**–**c**) and their one-step conversion into 3-aryl-8-hydroxy-3,4-dihydroisocoumarins (**5a**–**d**). In the present approach (Scheme 1) phthalide anions are generated from phthalides, and are then treated with benzyl bromides to obtain (±)-3-benzylphthalides in a single step. Thus, 7-methoxyphthalide **3a** on reaction with LDA in THF at −78 °C followed by treatment with 4-methoxybenzyl bromide furnished (±)-3-(4-methoxybenzyl)-7-methoxyphthalide **4a**, mp 108–109 °C, in 56% yield. The phthalide **3b** on similar reaction with LDA and 4-methoxybenzyl bromide provided (±)-3-(4-methoxybenzyl)-5,7-dimethoxyphthalide **1d**, mp 158–159 °C, in 54% yield. The aromatic protons of the phthalide ring of **1d** appeared as doublets (J = 2.0 Hz) at δ 6.17 and 6.39. These chemical shifts correspond to those (δ 6.11 and 6.29) reported[3] for the natural product (mp 78–80 °C), for which the structure **1e** was erroneously assigned. The aromatic protons of the phthalide ring in synthetic **1e** appear[9a] as singlets at δ 6.45 and 7.23. These chemical shifts are totally different to those reported for the natural phthalide. Hence the structure **1d** was assigned to the natural phthalide. Though there is a difference in the mps of the synthetic and the natural phthalide, the ^{1}H NMR and IR spectral data are identical. The difference in melting points could be due to polymorphism.

The phthalides **3b** and **3c** on similar reaction with benzyl bromides, in the presence of LDA, gave the 3-benzylphthalides **1b**, **4b** and **4c** in 40–56% yield. The ^{1}H NMR spectral properties of **1b** are identical with those reported for the natural *O*-methylbalantiolide.[1]

The 3-benzylphthalide **4a** on reaction with $AlCl_3$ in methylene dichloride at room temperature gave 4′-*O*-methylhydrangenol **5a**, mp 121–122 °C (lit.,[10c] mp 123 °C) in 77% yield. Its spectral properties are identical with those reported for the natural product. The novelty of this reaction is that it provides a (±)-3-aryl-8-hydroxy-3,4-dihydroisocoumarin in a single step from 7-methoxy-3-benzylphthalide. Selective demethylation of the 8-methoxy group of the isocoumarin also occurred in this step. 3-Benzylphthalides **1d** and **4b** on similar reaction with $AlCl_3$ gave 4′,6-*O,O*-dimethylthunberginol-C **5b** (63%) and the isocoumarin **5c** (73%), respectively. The 3-benzylphthalide **4c**

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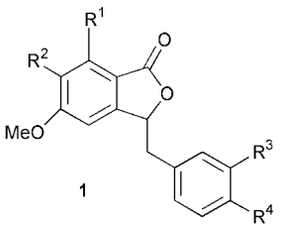
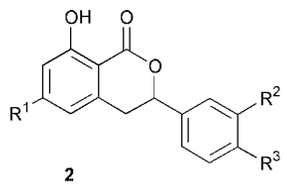


1	R^1	R^2	R^3	R^4
a	OH	H	OMe	OMe
b	OMe	H	OMe	OMe
c	OMe	H	OMe	OH
d	OMe	H	H	OMe
e	H	OMe	H	OMe
f	OH	OMe	OMe	OMe



2	R^1	R^2	R^3
a	H	H	OH
b	H	OH	OMe
c	OH	H	OH
d	OH	OH	OH
e	OH	OH	OMe
f	H	OH	OH

under similar conditions provided the 8-hydroxy-3,4-dihydroisocoumarin **5d** (63%) along with a minor amount of the 7-hydroxy-3-benzylphthalide **1f** (19%).

Conclusion

We have developed a simple and useful method for the synthesis of (±)-3-benzyl-7-methoxyphthalides from 7-methoxyphthalides and their single-step conversion into (±)-3-aryl-8-hydroxy-3,4-dihydroisocoumarins. This procedure can be used as an excellent alternative to previous syntheses of such compounds.

Experimental

All melting points are uncorrected. The IR spectra were recorded on a Perkin-Elmer FTIR-1615 spectrophotometer, and NMR spectra in $CDCl_3$ solutions on a JEOL FX 90Q (90 MHz), AC 200 Bruker (200 MHz) or Varian VXR 300S (300 MHz) spectrometer. Chemical shifts are expressed in δ (ppm) downfield from TMS as internal standard, and coupling constants J are in hertz. *n*-Butyllithium (prepared) was a 1.25 M solution in *n*-hexane, whose exact titre was determined by titration using diphenylacetic acid.[11] THF was distilled over $LiAlH_4$ before use. Phthalides **3a**–**c** were prepared according to the literature procedure.[12] Elemental analyses were obtained using Hosli's rapid carbon/hydrogen analyser. All reactions were performed in oven (125 °C)-dried glassware under an inert atmosphere of dry N_2.

General procedure for the synthesis of (±)-3-benzylphthalides (1b, 1d, 4a–c)

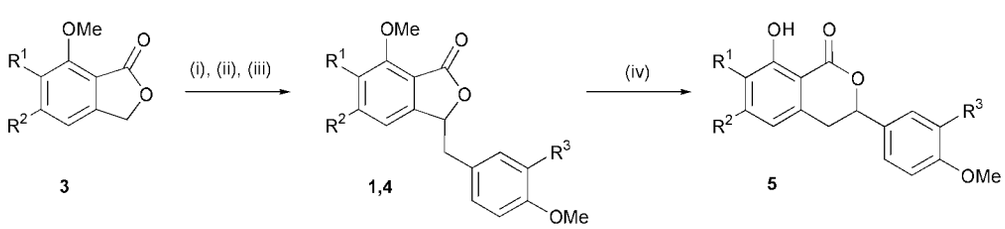
A solution of the appropriate phthalide **3** (1.30 mmol) in THF (10 mL) was added to a stirred solution of LDA (1.35 mmol) in THF (5 mL) at −78 °C under nitrogen atmosphere. The reaction mixture was stirred at −78 °C for 30 min and a solution of the corresponding benzyl bromide (1.35 mmol) in THF (5 mL) was added. Stirring was continued and the reaction mixture was allowed to come to room temperature during 2 h. Water (10 mL) was added to the reaction mixture. THF from the aqueous solution was removed *in vacuo.* The residue was acidified with dil. HCl and extracted with $CHCl_3$ (3 × 10 mL). The combined organic layers were washed with water and dried over Na_2SO_4. The gummy mass, obtained after evaporation of solvent, was purified by chromatography on silica gel, using EtOAc–hexane (3 : 7) as eluent, to give the (±)-3-benzylphthalides (**1b**, **1d** and **4a**–**c**).

(±)-3-(3,4-Dimethoxybenzyl)-5,7-dimethoxyphthalide (*O*-methylbalantiolide 1b). The anion generated from the phthalide **3b** on reaction with 3,4-dimethoxybenzyl bromide gave **1b** in 56% yield, mp 158 °C (lit.,[1] mp not mentioned); ν_{max}/cm^{-1} (Nujol) 1745; δ_H (300 MHz) 3.07 (dd, 1H, J = 13.5, 6.0, ArC*H*H), 3.17 (dd, 1H, J = 13.5, 6.1, Ar-CH*H*), 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.92 (s, 3H, OCH_3), 5.55 (t, 1H, J = 6.1, ArC*H*O), 6.20 (d, 1H, J = 1.0, ArH), 6.39 (d, 1H, J = 1.0, ArH), 6.72–6.80 (m, 3H, ArH) (Found: C, 66.45; H, 6.12. $C_{19}H_{20}O_6$ requires C, 66.27; H, 5.85%).

(±)-3-(4-Methoxybenzyl)-5,7-dimethoxyphthalide 1d. The anion generated from the phthalide **3b** on reaction with 4-methoxybenzyl bromide gave **1d**, in 54% yield, mp 158–159 °C; ν_{max}/cm^{-1} (Nujol) 1760; δ_H (200 MHz) 3.05, 3.10 (2 × dd, 2H, J = 14.0, 6.0, ArCH_2), 3.75 (s, 6H, 2 × OCH_3), 3.88 (s, 3H, OCH_3), 5.41 (t, 1H, J = 6.0, ArC*H*O), 6.17 (d, 1H, J = 2.0, ArH), 6.39 (d, 1H, J = 2.0, ArH), 6.77 (m, 2H, ArH), 7.08 (m, 2H, ArH) (Found: C, 68.50; H, 5.88. $C_{18}H_{18}O_5$ requires C, 68.78; H, 5.77%).

(±)-3-(4-Methoxybenzyl)-7-methoxyphthalide 4a. The anion generated from the phthalide **3a** on reaction with 4-methoxybenzyl bromide yielded **4a** in 56% yield, mp 108–109 °C; ν_{max}/cm^{-1} (Nujol) 1760; δ_H (90 MHz) 3.11 (d, 2H, J = 6.0, ArCH_2), 3.75 (s, 3H, OCH_3), 3.97 (s, 3H, OCH_3), 5.52 (t, 1H, J = 6.0, ArC*H*O), 6.63–7.25 (m, 6H, ArH), 7.52 (t, 1H, J = 8.0, ArH) (Found: C, 72.05; H, 5.54. $C_{17}H_{16}O_4$ requires C, 71.82; H, 5.67%).

(±)-3-(4-Methoxybenzyl)-5,6,7-trimethoxyphthalide 4b. The anion generated from the phthalide **3c** on reaction with 4-methoxybenzyl bromide furnished **4b** in 55% yield, mp 158 °C; ν_{max}/cm^{-1} (Nujol) 1738; δ_H (90 MHz) 3.07, 3.41 (2 × dd, 2H, J = 15.2, 6.3, ArCH_2), 3.78 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 4.09 (s, 3H, OCH_3), 5.44 (t, 1H, J = 6.3, ArC*H*O), 6.29 (s, 1H, ArH), 6.82 (m, 2H, ArH), 7.54 (m, 2H, ArH) (Found: C, 66.10; H, 6.02. $C_{19}H_{20}O_6$ requires C, 66.27; H, 5.85%).



3	R^1	R^2
a	H	H
b	H	OMe
c	OMe	OMe

	R^1	R^2	R^3
1b	H	OMe	OMe
1d	H	OMe	H
4a	H	H	H
4b	OMe	OMe	H
4c	OMe	OMe	OMe

5	R^1	R^2	R^3
a	H	H	H
b	H	OMe	H
c	OMe	OMe	H
d	OMe	OMe	OMe

Scheme 1 *Reagents and conditions*: (i) LDA, THF, −78 °C; (ii) ArCH $_2$X; (iii) H^+; (iv) $AlCl_3$, CH_2Cl_2.

(±)-3-(3,4-Dimethoxybenzyl)-5,6,7-trimethoxyphthalide 4c. The anion generated from the phthalide **3c** on reaction with 3,4-dimethoxybenzyl bromide gave **4c** in 40% yield, as a thick liquid; ν_{max}/cm^{-1} (Nujol) 1740; δ_H (90 MHz) 3.08, 3.50 (2 × dd, 2H, J = 14.0, 6.3, ArCH_2), 3.80 (s, 12H, 4 × OCH_3), 4.06 (s, 3H, OCH_3), 5.45 (t, 1H, J = 6.3, ArC*H*O), 6.27 (s, 1H, ArH), 6.72 (s, 3H, ArH) (Found: C, 64.01; H, 5.80. $C_{20}H_{22}O_7$ requires C, 64.16; H, 5.92%).

(±)-3-Aryl-8-hydroxy-3,4-dihydroisocoumarins 5a–d and the (±)-3-benzyl-7-hydroxyphthalide 1f: General procedure

A suspension of anhydrous $AlCl_3$ (196 mg, 1.47 mmol) in dry methylene dichloride (10 mL) was stirred at room temperature for 20 min. A solution of the appropriate (±)-3-benzylphthalide **1** or **4** (0.49 mmol) in methylene dichloride (10 mL) was added during in 5 min. The reaction mixture was stirred for 6 h (monitored by TLC) and poured slowly into ice-cold HCl (1 : 1 conc. HCl–water; 15 mL). The methylene dichloride layer was separated and the aqueous layer was extracted with methylene dichloride (2 × 15 mL). The combined organic extract was washed with water, dried (Na_2SO_4), and evaporated to give a solid. It was purified by chromatography over silica gel using EtOAc–hexane (1 : 9) as eluent to afford a solid, which on recrystallization from methylene dichloride–hexane provided the corresponding (±)-3-aryl-8-hydroxy-3,4-dihydroisocoumarins **5a**–**c**. In the case of **4c**, along with the isocoumarin **5d** the phthalide **1f** was also formed.

(±)-3-(4-Methoxyphenyl)-8-hydroxy-3,4-dihydroisocoumarin (4′-*O*-methylhydrangenol, 5a). The benzylphthalide **4a** on reaction with $AlCl_3$ provided the isocoumarin **5a** in 77% yield, mp 121–122 °C (lit.,[10c] 123 °C); ν_{max}/cm^{-1} (Nujol) 1675; δ_H (90 MHz) 3.08 (dd, 1H, J = 16.0, 5.0, C^4-H), 3.33 (dd, 1H, J = 16.0, 12.5, C^4-H), 3.80 (s, 3H, OCH_3), 5.55 (dd, 1H, J = 12.5, 5.0, C^3-H), 6.61–7.02 (m, 6H, ArH), 7.36 (t, 1H, J = 7.5, ArH), 11.05 (s, 1H, exchangeable with D_2O, OH) (Found: C, 71.28; H, 5.29. $C_{16}H_{14}O_4$ requires C, 71.10; H, 5.22%).

(±)-3-(4-Methoxyphenyl)-8-hydroxy-6-methoxy-3,4-dihydroisocoumarin (4′,6-*O*,*O*-dimethylthunberginol-C, 5b). The benzylphthalide **1d** on reaction with $AlCl_3$ provided **5b** in 63% yield, mp 118–119 °C; ν_{max}/cm^{-1} (Nujol) 1655; δ_H (90 MHz) 3.05 (dd, 1H, J = 16.0, 5.0, C^4-H), 3.33 (dd, 1H, J = 16.0, 12.5, C^4-H), 3.80 (s, 6H, 2 × OCH_3), 5.47 (dd, 1H, J = 12.5, 5.0, C^3-H), 6.36 (s, 1H, ArH), 6.41 (s, 1H, ArH), 6.91 (d, 1H, J = 7.5, ArH), 8.22 (d, 1H, J = 7.5, ArH), 11.22 (s, 1H, exchangeable with D_2O, OH) (Found: C, 68.13; H, 5.59. $C_{17}H_{16}O_5$ requires C, 67.99; H, 5.37%).

(±)-3-(4-Methoxyphenyl)-8-hydroxy-6,7-dimethoxy-3,4-dihydroisocoumarin 5c. The benzylphthalide **4b** on reaction with $AlCl_3$ furnished **5c** in 73% yield, mp 175 °C; ν_{max}/cm^{-1} (Nujol) 3350, 1660; δ_H (90 MHz) 3.04 (dd, 1H, J = 15.2, 3.8, C^4-H), 3.32 (dd, 1H, J = 15.2, 11.4, C^4-H), 3.80 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 5.47 (dd, 1H, J = 11.4, 3.8, C^3-H), 6.29 (s, 1H, ArH), 6.91 (m, 2H, ArH), 7.36 (m, 2H, ArH), 11.07 (s, 1H, exchangeable with D_2O, OH) (Found: C, 65.54; H, 5.60. $C_{18}H_{18}O_6$ requires C, 65.44; H, 5.49%).

(±)-3-(3,4-Dimethoxyphenyl)-8-hydroxy-6,7-dimethoxy-3,4-dihydroisocoumarin 5d and (±)-3-(3,4-dimethoxybenzyl)-7-hydroxy-5,6-dimethoxyphthalide 1f. The benzylphthalide **4c** on reaction with $AlCl_3$ gave **5d** and **1f** in 63 and 19% yield, respectively. Compound **5d** had mp 148 °C; ν_{max}/cm^{-1} (Nujol) 3409, 1661; δ_H (90 MHz) 3.07 (dd, 1H, J = 15.2, 3.8, C^4-H), 3.35 (dd, 1H, J = 15.2, 11.4, C^4-H), 3.87 (s, 12H, 4 × OCH_3), 5.47 (dd, 1H, J = 11.4, 3.8, C^3-H), 6.32 (s, 1H, ArH), 6.95 (s, 3H, ArH), 11.08 (s, 1H, exchangeable with D_2O, OH) (Found: C, 63.11; H, 5.79. $C_{19}H_{20}O_7$ requires C, 63.33; H, 5.59%).

Compound **1f** was a viscous liquid; ν_{max}/cm^{-1} (nujol) 3340, 1740; δ_H (90 MHz) 3.07–3.18 (m, 2H, ArCH_2), 3.80 (s, 12H, 4 × OCH_3), 5.50 (t, 1H, J = 6.3, ArC*H*O), 6.29 (s, 1H, ArH), 6.34 (s, 1H, exchangeable with D_2O, OH), 6.72 (s, 3H, ArH) (Found: C, 63.22; H, 5.65. $C_{19}H_{20}O_7$ requires C, 63.33; H, 5.59%).

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