Synthesis of 6-Methoxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene, a Synthetic Intermediate of a Linear Abietane Diterpene, Umbrosone

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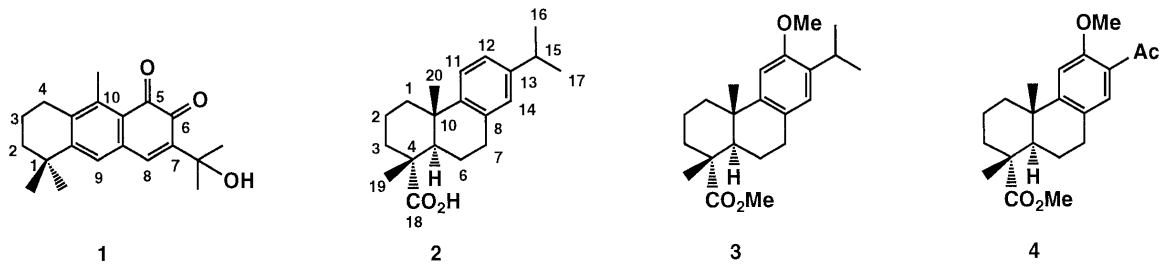
Methyl 13-acetyl-12-methoxy-8,11,13-podocarpatrien-18-oate, prepared from (+)-dehydroabietic acid, was converted into methyl 12-methoxy-7-oxo-5,8,11,13-podocarpatetraen-18-oate (9) by a series of reactions: haloform reaction, decarboxylation, Jones oxidation, and dehydrogenation. Reduction of 9 with sodium borohydride, followed by treatment of the resulting 7-hydroxy compound with boron trifluoride etherate, afforded a rearranged ester, methyl 6-methoxy-1,10-dimethyl-1,2,3,4-tetrahydroanthracene-1-carboxylate. This was further converted into 6-methoxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene (14) by means of the following reactions: lithium aluminum hydride reduction, pyridinium chlorochromate oxidation, and Huang-Minlon reduction. Compound 14 was finally converted into the desired orthoquinone (1) according to the procedure of Ghosh and Ghatak. The synthetic 1 was shown to be identical with natural umbrosone by spectral comparisons.

Key words synthesis; umbrosone; diterpene; *Hyptis umbrosa*; (+)-dehydroabietic acid

Umbrosone (**1**), an unusual natural diterpene orthoquinone possessing a rearranged linear abietane skeleton, was isolated from the roots of *Hyptis umbrosa* SALZM (Lamiaceae) by Monache *et al.*[1] and showed a significant antimicrobial activity.[1] This biological activity prompted us to study the synthesis of umbrosone, although its first total synthesis was recently reported by Ghosh and Ghatak.[2] In this paper, we describe a new synthesis of umbrosone (**1**) starting from (+)-dehydroabietic acid (**2**), which is easily available from pine rosin. The pivotal step in our present synthesis involves a novel skeletal rearrangement of a hydrophenanthrene into a hydroanthracene.

According to our previous method,[3] (+)-dehydroabietic acid (**2**) was first converted into methyl 13-acetyl-12-methoxy-8,11,13-podocarpatrien-18-oate (**4**) *via* the intermediate methyl 12-methoxy-8,11,13-abietatrien-18-oate (**3**) (Fig. 1).

Haloform reaction of the acetyl compound (**4**) with bromine and aqueous potassium hydroxide in 1,4-dioxane afforded a carboxylic acid derivative (**5**: 86.2% yield), which was then submitted to decarboxylation with copper powder in refluxing quinoline to give methyl 12-hydroxy-8,11,13-podocarpatrien-18-oate (**6**[4]: 48.7% yield) and its methyl ether (**7**[4]: 38.2% yield). The phenolic compound **6** was easily converted into the methyl ether **7** with methyl iodide and anhydrous potassium carbonate in refluxing ethyl methyl ketone, in 96.1% yield. Oxidation of **7** with Jones reagent in acetone at room temperature afforded a 7-oxo compound (**8**: 85.1% yield), which was converted into an enone derivative (**9**: 79.5% yield) by refluxing with selenium dioxide in aqueous acetic acid. The IR spectrum of **9** showed absorption bands at 1720 and 1640 cm^{-1} due to a methoxycarbonyl group and an α,β-unsaturated carbonyl group. In the ^{1}H-NMR spectrum, the enone **9** showed signals at δ 1.53 (3H, s) and 1.64 (3H, s) due to two tertiary methyl groups, at δ 3.72 (3H, s) due to a methoxycarbonyl group, at δ 3.89 (3H, s) due to a methoxyl group, at δ 6.12 (1H, s) due to an olefinic proton, and at δ 6.92 (1H, dd, J=9.7, 2.4 Hz), 6.98 (1H, br s, overlap), 8.11 (1H, d, J=9.7 Hz) due to three aromatic protons. The enone **9** was reduced with sodium borohydride in the presence of cerium(III) chloride heptahydrate[5] at 0—3 °C and the resulting 7-hydroxy compound (**10**) was then treated with boron trifluoride etherate in dichloromethane at room temperature to give an optically active rearranged ester (**11**), $[\alpha]_D$ −0.99° ($CHCl_3$), in 66.6% yield from **9**. The mass spectrum of **11** gave a molecular ion peak at m/z 298.1599 (M^+), corresponding to the formula $C_{19}H_{22}O_3$. In the ^{1}H-NMR spectrum, the ester **11** exhibited the presence of a tertiary methyl group at δ 1.65 (3H, s), a methyl group on an aryl ring at δ 2.52 (3H, s), a methoxycarbonyl group at δ 3.65 (3H, s), a methoxyl group at δ 3.92 (3H, s), and four



1 2 3 4

Fig. 1

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aromatic protons at δ 7.07 (1H, dd, J=8.8, 2.4 Hz), 7.23 (1H, d, J=2.4 Hz), 7.52 (1H, s), 7.64 (1H, d, J=8.8 Hz). Differential nuclear Overhauser effects (NOE's) of **11** were observed between a methyl signal at δ 1.65 and an aromatic proton signal at δ 7.52, between an aryl methyl signal at δ 2.52 and a methylene signal at δ 2.79—2.95 (2H, m) and a *meta*-coupling aromatic proton signal at δ 7.23, between a methoxyl signal at δ 3.92 and aromatic proton signals at δ 7.07 and 7.23, and between an aromatic proton signal at δ 7.52 and a methyl signal at δ 1.65 and an aromatic proton signal at δ 7.64, as shown in Fig. 2. Since the ester **11** showed optical activity, the stereochemistry of the C-1 position in **11** was assigned to be the same as that of the C-4 position in the enone **9**. From these spectral data, the structure of **11** was assigned as methyl 6-methoxy-1,10-dimethyl-1,2,3,4-tetrahydroanthracene-1-carboxylate (Chart 1).

Subsequently, conversion of a methoxycarbonyl group in **11** into a methyl group was carried out as follows. The ester **11** was reduced with lithium aluminum hydride in refluxing tetrahydrofuran to give an alcohol **12** $[\alpha]_D$ $-17.5°$ ($CHCl_3$) in 98.9% yield. Oxidation of **12** with pyridinium chlorochromate in dichloromethane at room temperature, followed by Huang–Minlon reduction of the resulting formyl compound **13** (82.1% yield) $[\alpha]_D$ $-10.8°$ ($CHCl_3$) afforded a *gem*-dimethyl compound **14** in 87.9% yield. The mass spectrum of **14** gave a molecular ion peak at m/z 254.1665 (M^+), corresponding to the formula $C_{18}H_{22}O$. In the ^{1}H-NMR spectrum, compound **14** exhibited the presence of two tertiary methyl groups at δ 1.38 (6H, s), a methyl group on an aryl ring at δ 2.51 (3H, s), a methoxyl group at δ 3.92 (3H, s), and four aromatic protons at δ 7.05 (1H, dd, J=8.8, 2.3 Hz), 7.22 (1H, br s), 7.65 (1H, s), 7.66 (1H, d, J=8.8 Hz). These spectral data suggested the structure of **14** to be 6-methoxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene. Since this compound (**14**) was used as an intermediate by Ghosh and Ghatak[2] to synthesize umbrosone (**1**), our present synthesis of **14** represents a formal synthesis of umbrosone (**1**).

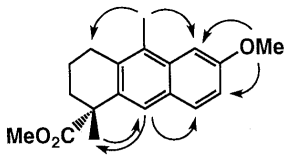
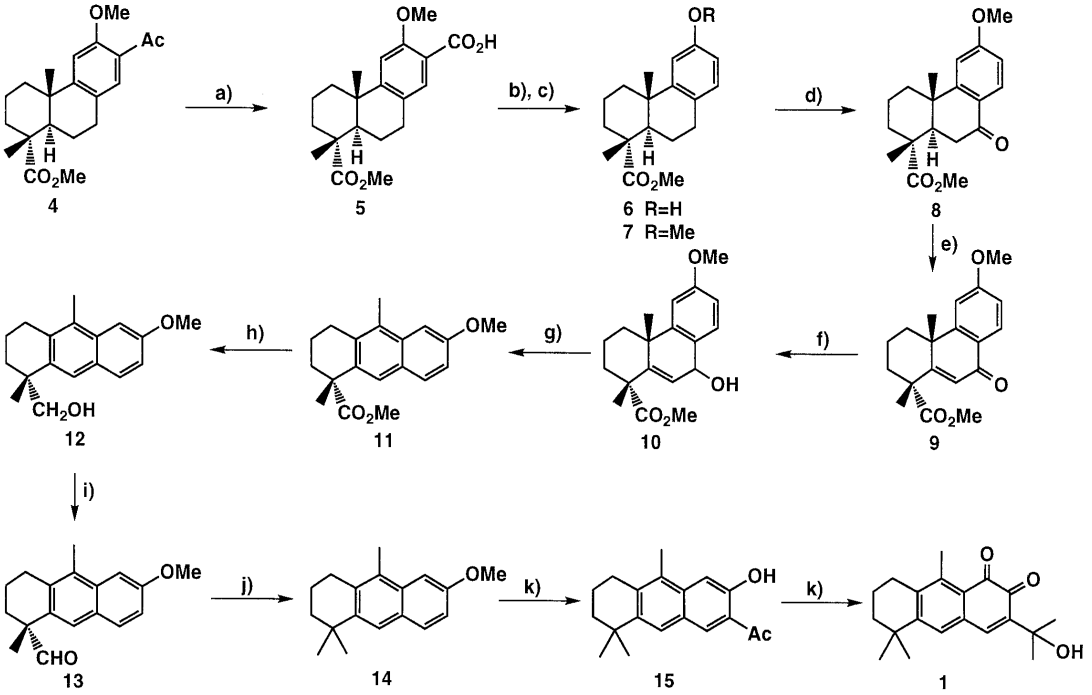


Fig. 2. NOE of Rearranged Compound **11**

According to the procedure of Ghosh and Ghatak,[2] **14** was finally converted into umbrosone (**1**) *via* 7-acetyl-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracen-6-ol (**15**). The synthetic **1** (mp 164—166 °C) was shown to be identical with natural umbrosone (mp 163—165 °C) by spectral comparisons.

A possible mechanism for the skeletal rearrangement of the enone **9** into the ester **11** is depicted in Chart 2. The enone **9** is first transformed into a C-5 carbonium ion intermediate (**10a**) by sodium borohydride reduction and subsequent treatment of the resulting 7-hydroxy compound (**10**) with boron trifluoride etherate. The migration of the C(1)–C(10) bond in **10a** to the C-5 position provides a C-10 carbonium ion intermediate, which is isomerized to a spiro intermediate (**10b**). Subsequent migration of the C(4)–C(5) bond in **10b** to the C-6 position results in the formation of a new carbonium ion intermediate (**10c**), which is then transformed into the optically active ester **11** by deprotonation.



Reagents a) Br_2, aq.KOH b) Cu, quinoline c) MeI, K_2CO_3 d) Jones reagent e) SeO_2 f) $NaBH_4$, $CeCl_3 \cdot 7H_2O$ g) $BF_3 \cdot OEt_2$ h) $LiAlH_4$ i) pyridinium chlorochromate j) $NH_2NH_2 \cdot H_2O$;NaOH k) lit. 2

Chart 1

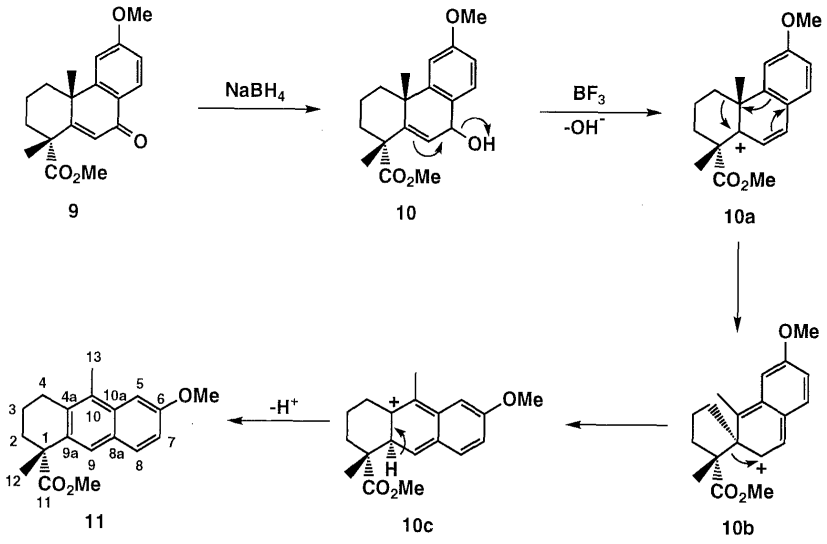


Chart 2

Experimental

All melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. The IR spectra were measured on a Shimadzu IR-400 spectrometer in chloroform. The mass spectra were recorded on a JEOL JMS-SX102A spectrometer. The ^{1}H-NMR spectra were recorded with a Hitachi R-1500 (60 MHz) or a JEOL JNM EX-400 (400 MHz) spectrometer in deuteriochloroform using tetramethylsilane as an internal standard unless otherwise stated, and the following abbreviations are used: s=singlet, d=doublet, dd=double doublet, t=triplet, m=multiplet, br=broad. Column chromatography was performed using Merck silica gel (0.063—0.200 mm).

12-Methoxy-18-methoxycarbonyl-8,11,13-podocarpatrien-13-oic Acid (5) Bromine (1.91 ml) was added dropwise to stirred aqueous potassium hydroxide (20%, 40 ml) at 2—7 °C over a 4-min period. After the addition of a solution of methyl 13-acetyl-12-methoxy-8,11,13-podocarpatrien-18-oate[3] (**4**) (4.138 g) in 1,4-dioxane (80 ml) at 3—12 °C over a 5-min period, the mixture was stirred at room temperature for 1 h and then refluxed for 1 h. It was cooled, diluted with water, and washed with ether to remove unchanged acetyl compound (**4**). The aqueous phase was acidified with dilute hydrochloric acid and extracted with ether. The ether solution was washed successively with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (Mallinckrodt CC-4, 50 g), using ether–benzene (1 : 9) as an eluent, to give **5** (3.586 g, 86.2% yield). This was recrystallized from a mixture of acetone and hexane, mp 156—158 °C, $[\alpha]_D$ +69.0° ($CHCl_3$, c=2.51). IR: 3525, 3280, 1720, 1615 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.24 (3H, s), 1.29 (3H, s) (C4-CH_3, C10-CH_3), 3.69 (3H, s, $-CO_2CH_3$), 4.04 (3H, s, $-OCH_3$), 6.90 (1H, s, C11-H), 7.85 (1H, s, C14-H). HR-MS m/z: Found: 346.1786 (M^+). Calcd for $C_{20}H_{26}O_5$: M, 346.1780.

Methyl 12-Hydroxy-8,11,13-podocarpatrien-18-oate (6) and Its Methyl Ether (7) a) A stirred mixture of **5** (180 mg) and copper powder (90 mg) in quinoline (1.8 ml) was gently refluxed for 1 h, cooled, and then filtered to remove copper powder. The filtrate was acidified with dilute hydrochloric acid and extracted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using benzene as an eluent, to give **7** as an oil (60 mg, 38.2% yield), $[\alpha]_D$ +66.0° ($CHCl_3$, c=4.26). IR: 1710, 1610 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.22 (3H, s), 1.27 (3H, s) (C4-CH_3, C10-CH_3), 3.66 (3H, s, $-CO_2CH_3$), 3.77 (3H, s, $-OCH_3$), 6.65 (1H, dd, J=8.2, 2.6 Hz, C13-H), 6.80 (1H, d, J=2.6 Hz, C11-H), 6.96 (1H, d, J=8.2 Hz, C14-H). HR-MS m/z: Found: 302.1900 (M^+). Calcd for $C_{19}H_{26}O_3$: M, 302.1882.

Further elution with ether–benzene (1 : 9) afforded **6** (73 mg, 48.7% yield). This was recrystallized from a mixture of acetone and hexane, mp 189—192 °C (lit.[4] mp 186—189 °C), $[\alpha]_D$ +71.3° ($CHCl_3$, c=2.05). IR: 3605, 3375, 1710, 1610 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.19 (3H, s), 1.27 (3H, s) (C4-CH_3, C10-CH_3), 3.68 (3H, s, $-CO_2CH_3$), 5.23 (1H, br, –OH), 6.57 (1H, dd, J=8.2, 2.4 Hz, C13-H), 6.73 (1H, d, J=2.4 Hz, C11-H), 6.89 (1H, d, J=8.2 Hz, C14-H). HR-MS m/z: Found: 288.1727 (M^+). Calcd for $C_{18}H_{24}O_3$: M, 288.1725.

b) A stirred mixture of **6** (350 mg), methyl iodide (0.7 ml), and anhydrous potassium carbonate (1.1 g) in ethyl methyl ketone (5.0 ml) was gently refluxed for 8 h. The mixture was diluted with water and extracted with ether. The ether solution was washed successively with aqueous sodium thiosulfate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using benzene as an eluent, to give **7** (317 mg, 96.1% yield), whose IR and ^{1}H-NMR spectra were identical with those of an authentic sample.

Methyl 12-Methoxy-7-oxo-8,11,13-podocarpatrien-18-oate (8) Jones reagent (2.5 mol dm^{-3}, 5.4 ml) was added to a stirred solution of **7** (1.625 g) in acetone (20 ml) with cooling in an ice-water bath over a 3-min period. The mixture was stirred at this temperature for 5 min, further stirred at room temperature for 2 h, and then diluted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (30 g), using benzene as an eluent, to give the starting **7** (204 mg). Further elution with ether–benzene (1 : 9) afforded **8** as an oil (1.446 g, 85.1% yield), $[\alpha]_D$ +38.1° ($CHCl_3$, c=3.74). IR: 1720, 1665 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.26 (3H, s), 1.34 (3H, s) (C4-CH_3, C10-CH_3), 2.67 (2H, dd, J=11.3, 4.8 Hz, C6-H_2), 3.66 (3H, s, $-CO_2CH_3$), 3.86 (3H, s, $-OCH_3$), 6.80 (1H, dd, J=8.7, 2.4 Hz, C13-H), 6.84 (1H, d, J=2.4 Hz, C11-H), 8.01 (1H, d, J=8.7 Hz, C14-H). HR-MS m/z: Found: 316.1670 (M^+). Calcd for $C_{19}H_{24}O_4$: M, 316.1675.

Methyl 12-Methoxy-7-oxo-5,8,11,13-podocarpatetraen-18-oate (9) A stirred mixture of **8** (1.308 g) and selenium dioxide (95%, 6.54 g) in acetic acid (26 ml) and water (13 ml) was refluxed for 17.5 h. The cooled mixture was filtered and the filtrate was evaporated *in vacuo*. The residue was extracted with ether. The ether solution was washed successively with aqueous sodium hydrogen carbonate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (30 g), using ether–benzene (5 : 95) as an eluent, to give **9** as an oil (1.033 g, 79.5% yield), $[\alpha]_D$ +90.6° ($CHCl_3$, c=2.19). IR: 1720, 1640 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.53 (3H, s), 1.64 (3H, s) (C4-CH_3, C10-CH_3), 3.72 (3H, s, $-CO_2CH_3$), 3.89 (3H, s, $-OCH_3$), 6.12 (1H, s, C6-H), 6.92 (1H, dd, J=9.7, 2.4 Hz, overlap, C13-H), 6.98 (1H, br s, overlap, C11-H), 8.11 (1H, d, J=9.7 Hz, C14-H). HR-MS m/z: Found: 314.1520 (M^+). Calcd for $C_{19}H_{22}O_4$: M, 314.1518.

Rearrangement of Methyl 12-Methoxy-7-oxo-5,8,11,13-podocarpatetraen-18-oate (9) Sodium borohydride (91 mg) was added to a stirred mixture of **9** (720 mg) and cerium(III) chloride heptahydrate (896 mg) in methanol and tetrahydrofuran (1 : 1, 11 ml) at 0—3 °C over a 3-min period. The mixture was further stirred at this temperature for 10 min, diluted with ether, washed with brine, dried over sodium sulfate, and evaporated *in vacuo* to give a crude alcohol (**10**, 740 mg). IR: 3500, 3230, 1720 cm^{-1}.

A mixture of the above crude alcohol **10** (740 mg) and boron trifluoride etherate (0.8 ml) in dichloromethane (17 ml) was stirred at room temperature for 3 h. The mixture was diluted with ether, washed

successively with dilute hydrochloric acid and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (50 g), using benzene as an eluent, to give an oily ester (**11**, 455 mg: 66.6% yield from **9**), $[\alpha]_D$ −0.99° ($CHCl_3$, c=3.25). IR: 1720, 1630, 1600 cm^{-1}. ^{1}H-NMR (400 MHz) δ: 1.65 (3H, s, C1-CH_3), 1.74—1.81 (1H, m), 2.32—2.39 (1H, m) (C2-H_2), 1.87—2.02 (2H, m, C3-H_2), 2.52 (3H, s, C10-CH_3), 2.79—2.95 (2H, m, C4-H_2), 3.65 (3H, s, $-CO_2CH_3$), 3.92 (3H, s $-OCH_3$), 7.07 (1H, dd, J=8.8, 2.4 Hz, C7-H), 7.23 (1H, d, J=2.4 Hz, C5-H), 7.52 (1H, s, C9-H), 7.64 (1H, d, J=8.8 Hz, C8-H). ^{13}C-NMR (100 MHz, $CDCl_3$) δ: 14.4 (13-C), 19.8 (3-C), 28.2 (4-C), 28.2 (12-C), 34.6 (2-C), 46.9 (1-C), 52.2 ($CO_2\underline{C}H_3$), 55.1 ($O\underline{C}H_3$), 102.0 (5-C), 117.3 (7-C), 124.7 (9-C), 129.86 (8-C), 127.4, 129.92, 132.4, 132.8, 135.5 (4a-, 8a-, 9a-, 10a-, 10-C), 157.5 (6-C), 178.0 (11-C). HR-MS m/z: Found: 298.1599 (M^+). Calcd for $C_{19}H_{22}O_3$: M, 298.1569.

6-Methoxy-1,10-dimethyl-1,2,3,4-tetrahydroanthracene-1-methanol (12) Lithium aluminum hydride (76 mg) was added to a stirred solution of **11** (398 mg) in dry tetrahydrofuran (10 ml) with cooling in a water bath over a 3-min period. The mixture was gently refluxed for 2 h, cooled, poured into ice-dilute hydrochloric acid, and extracted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (15 g), using chloroform as an eluent, to give an oily alcohol (**12**, 357 mg: 98.9% yield), $[\alpha]_D$ −17.5° ($CHCl_3$, c=2.50). IR: 3580, 3430, 3230, 1630, 1600 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.34 (3H, s, C1-CH_3), 1.70—2.26 (4H, m, C2-H_2, C3-H_2), 2.51 (3H, s, C10-CH_3), 2.89 (2H, br t, J=5.6 Hz, C4-H_2), 3.72 (2H, dd, J=19.9, 11.1 Hz, $-C\underline{H}_2OH$), 3.92 (3H, s, $-OCH_3$), 7.07 (1H, dd, J=8.8, 2.3 Hz, C7-H), 7.23 (1H, br s, C5-H), 7.59 (1H, s, C9-H), 7.66 (1H, d, J=8.8 Hz, C8-H). HR-MS m/z: Found: 270.1602 (M^+). Calcd for $C_{18}H_{22}O_2$: M, 270.1620.

6-Methoxy-1,10-dimethyl-1,2,3,4-tetrahydroanthracene-1-carbaldehyde (13) A mixture of **12** (350 mg) and pyridinium chlorochromate (558 mg) in dichloromethane (14 ml) was stirred at room temperature for 3 h. The mixture was diluted with ether, washed successively with aqueous sodium hydrogen carbonate and brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using chloroform as an eluent, to give an aldehyde **13** (282 mg, 82.1% yield), mp 105—106° C (from hexane), $[\alpha]_D$ −10.8° ($CHCl_3$, c=2.74). IR: 2710, 1710, 1625, 1600 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.50 (3H, s, C1-CH_3), 1.77—2.25 (4H, m, C2-H_2, C3-H_2), 2.53 (3H, s, C10-CH_3), 2.93 (2H, br t, J=5.7 Hz, C4-H_2), 3.94 (3H, s, $-OCH_3$), 7.09 (1H, dd, J=8.8, 2.4 Hz, C7-H), 7.25 (1H, s, C5-H), 7.35 (1H, s, C9-H), 7.66 (1H, d, J=8.8 Hz, C8-H), 9.54 (1H, s, –CHO). HR-MS m/z: Found: 268.1456 (M^+). Calcd for $C_{18}H_{20}O_2$: M, 268.1463.

6-Methoxy-1,1,10-trimethyl-1,2,3,4-tetrahydroanthracene (14) A mixture of **13** (240 mg) and hydrazine hydrate (1.2 ml) in diethylene glycol (6.0 ml) was refluxed for 2 h, then powdered sodium hydroxide (1.20 g) was added. The reaction mixture was heated at 175—185 °C for 2 h, cooled, diluted with water, and extracted with ether. The ether solution was washed with brine, dried over sodium sulfate, and evaporated *in vacuo*. The residue was chromatographed on silica gel (10 g), using hexane–chloroform (7 : 3) as an eluent, to give a colorless solid **14** (200 mg, 87.9% yield), mp 112—113 °C (from hexane) (lit.[2] mp 110 °C). IR: 1630, 1600 cm^{-1}. ^{1}H-NMR (60 MHz) δ: 1.38 (6H, s, C1-$(CH_3)_2$), 2.51 (3H, s, C10-CH_3), 2.90 (2H, t, J=9.0 Hz, C4-H_2), 3.92 (3H, s, $-OCH_3$), 7.05 (1H, dd, J=8.8, 2.3 Hz, C7-H), 7.22 (1H, br s, C5-H), 7.65 (1H, s, C9-H), 7.66 (1H, d, J=8.8 Hz, C8-H). HR-MS m/z: Found: 254.1665 (M^+). Calcd for $C_{18}H_{22}O$: M, 254.1671.

Umbrosone (1) According to the procedure of Ghosh and Ghatak,[2] compound **14** was converted into an orthoquinone (**1**), mp 164—166 °C (dark red crystals from acetone–hexane). IR: 3520, 3275, 1680, 1650, 1580 cm^{-1}. ^{1}H-NMR (400 MHz) δ: 1.32 (6H, s, C1-$(CH_3)_2$), 1.55 (6H, s, C7-C$(C\underline{H}_3)_2$OH), 1.65 (2H, m, C2-H_2), 1.85 (2H, m, C3-H_2), 2.58 (3H, s, C10-CH_3), 2.69 (2H, t, J=6.4 Hz, C4-H_2), 3.25 (1H, br, –OH), 7.18 (1H, s, C9-H), 7.40 (1H, s, C8-H). HR-MS m/z: Found: 312.1715 (M^+). Calcd for $C_{20}H_{24}O_3$: M, 312.1725. The synthetic **1** was shown to be identical with natural umbrosone (mp 163—165 °C)[2] by spectral comparisons.

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