Studies on the Flavonoid Components of *Lindera umbellata* THUNB. var. *membranacea* (MAXIM.) MOMIYAMA[1)]

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A new chalcone, linderachalcone, and two new flavanones, methyllinderatone and isolinderatone, were isolated from the leaves of *Lindera umbellata* THUNB. var. *membranacea* (MAXIM.) MOMIYAMA. Their structures were established by chemical and spectroscopic means.

Keywords *Lindera umbellata* var. *membranacea*; Lauraceae; linderachalcone; methyllinderatone; isolinderatone; chalcone; flavanone; *p*-menthene; rubranine

Previously,[2)] we reported the isolation and the structural elucidation of two novel flavonoids, linderatin (**1**) and linderatone (**2**), from the leaves of *Lindera umbellata* THUNB. var. *lancea* MOMIYAMA and *L. umbellata* THUNB., and further the synthesis of (±)-**1**. Both compounds are novel flavonoids having a *p*-menthene substituent. In the course of further investigation of the varieties of *L. umbellata*, we isolated a new chalcone, linderachalcone (**3**),[3)] and two new flavanone derivatives, methyllinderatone (**4**)[1)] and isolinderatone (**5**),[1)] from the fresh leaves of *L. umbellata* THUNB. var. *membranacea* (MAXIM.) MOMIYAMA. We now wish to describe the structure elucidation of the two flavonoids (**4** and **5**).

Methyllinderatone (**4**), $C_{26}H_{30}O_4$, gave a bluish color with ethanolic ferric chloride and was positive to the magnesium–hydrochloric acid test. The infrared (IR) spectrum revealed the presence of hydroxyl (3600 cm^{-1}) and conjugated carbonyl (1630 cm^{-1}) groups. In the proton nuclear magnetic resonance (^{1}H-NMR) spectrum, signals of three methyl groups (δ 0.79 and 0.84, 6H, d × 2, J=7 Hz; δ 1.66, 3H, br s), methylene protons adjacent to a carbonyl group (δ 2.76, 1H, dd, J=4, 17 Hz; δ 3.10, 1H, dd, J=13, 17 Hz), a methoxyl group (δ 3.77, 3H, s), an olefinic proton (δ 5.16, 1H, br s), a methine proton (δ 5.43, 1H, dd, J=4, 13 Hz), an aromatic proton (δ 6.08, 1H, s), a phenyl group (δ 7.44, 5H, s), and a hydroxyl group (δ 12.34, 1H, s) were observed. The carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectrum indicated the presence of twenty-six carbons (Table I).

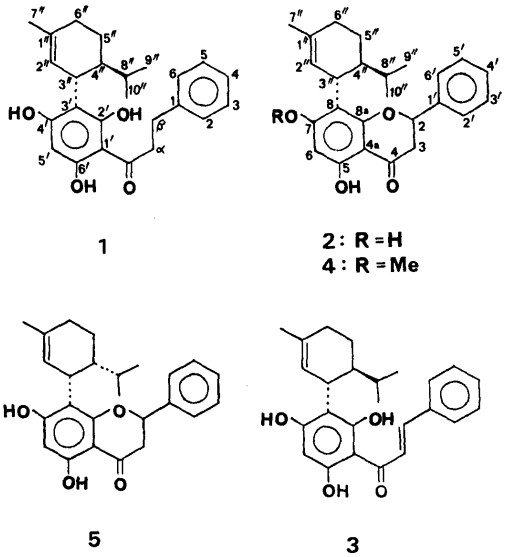

Chart 1

The mass spectrum (MS) of methyllinderatone showed a molecular ion at *m/z* 406 indicating an increase of fourteen mass units in comparison with linderatone (**2**). This spectrum also had the characteristic peak at *m/z* 336 which was formed by the retro Diels–Alder reaction[4)] of a *p*-menthene unit as in **2**. The ^{1}H-NMR and ^{13}C-NMR spectra of this compound were very similar to those of **2** except for the signals (δ 3.77 in ^{1}H-NMR and δ 56.4 in ^{13}C-NMR) due to a methoxyl function. These results suggest that **4** may be a 7-*O*-methyl ether of **2**. Treatment of **2** with diazomethane in ether afforded a monomethyl derivative which was identical with methyllinderatone (IR, ^{1}H-NMR, MS, co-thin layer chromatography (co-TLC) in a variety of solvent systems). Therefore, the structure of methyllinderatone is shown to be **4**.

Isolinderatone (**5**), $C_{25}H_{28}O_4$, gave a bluish color with

TABLE I. ^{13}C-NMR Data for **1**, **2**, **4**, and **5** in Acetone-d_6

Carbon[a)]	1	2	4	5	Carbon[a)]
C-1	143.2	139.9	140.1	140.2	C-1′
C-2	129.4	129.2	129.5	129.2	C-2′
C-3	129.6	127.1	127.3	129.1	C-3′
C-4	127.1	126.2	126.5	127.0	C-4′
C-5	129.6	127.1	127.3	129.1	C-5′
C-6	129.4	129.2	129.5	129.2	C-6′
C-1′	105.4	103.0	103.6	103.5	C-4a
C-2′	161.4[b)]	161.7[b)]	162.2[b)]	162.1[b)]	C-8a
C-3′	110.5	111.8	113.3	110.7	C-8
C-4′	163.9[b)]	163.3[b)]	167.4[b)]	163.1[b)]	C-7
C-5′	95.8	95.8	92.1	96.8	C-6
C-6′	165.9[b)]	165.6[b)]	162.6[b)]	165.6[b)]	C-5
C=O	205.9	196.7	197.4	197.5	C-4
C-α	46.6	43.7	43.8	43.8	C-3
C-β	31.5	79.7	80.1	79.9	C-2
OMe	—	—	56.4	—	OMe
C-1″	135.4	134.0	132.5	133.5	C-1″
C-2″	126.9	126.2	126.5	126.4	C-2″
C-3″	36.0	35.7	35.9	36.3	C-3″
C-4″	43.0	42.4	42.4	43.2	C-4″
C-5″	23.7	23.6	23.6	23.5	C-5″
C-6″	31.5	31.4	31.5	30.3	C-6″
C-7″	23.7	23.9	23.9	23.5	C-7″
C-8″	29.1	29.1	29.3	29.3	C-8″
C-9″	16.9	16.7	16.7	16.7	C-9″
C-10″	22.0	21.9	21.8	21.9	C-10″

a) For numbering systems, see Chart 1. *b*) Assignments may be interchanged in each column.

ethanolic ferric chloride and was positive to the magnesium–hydrochloric acid test. The IR spectrum indicated the presence of hydroxyl (3370 cm^{-1}) and conjugated carbonyl (1640 cm^{-1}) groups. In the ^{1}H-NMR spectrum, signals of three methyl groups (δ 0.55 and 0.79, 6H, d×2, J=7 Hz; δ 1.77, 3H, br s), methylene protons adjacent to a carbonyl group (δ 2.75, 1H, dd, J=4, 17 Hz; δ 3.07, 1H, dd, J=13, 17 Hz), two methine protons (δ 3.66—3.92, 1H, m; δ 5.30, 1H, dd, J=4, 13 Hz), an olefinic proton (δ 5.50, 1H, br s), an aromatic proton (δ 6.04, 1H, s), a phenyl group (δ 7.39, 5H, s), and a hydroxyl group (δ 12.34, 1H, s) were observed.

The MS of **5** showed the same molecular ion as **2** at m/z 392 and also had a characteristic peak at m/z 322 which was formed by the retro Diels–Alder reaction of a *p*-menthene unit as in **3** and **4**. The ^{13}C-NMR spectrum of **5** was similar to that of **2** except for some signals due to the carbons of a monoterpene unit (Table I). The ^{1}H-NMR spectrum also showed close similarity to that of **2** except that the geminal methyl groups (δ 0.55 and 0.79) were observed at extremely high field. This compound also seemed to be a 5,7-dihydroxyflavanone having a monoterpene substituent on the A ring. The stereochemistry of the flavanone ring of **5** was 2*S*, as the circular dichroism (CD) spectrum of this compound exhibits characteristic Cotton effects for 2*S* flavanones.[5] The negative result of the Gibbs test and the bathochromic shift[6] in the ultraviolet (UV) spectrum suggest that **3** has a *p*-menthene substituent, not on the C-6 but on the C-8 position in the A ring, as discussed[7] in the case of **2** in the previous paper.

Next, from careful investigation of the ^{1}H-NMR spectra, we found that the signal of $C_{3''}$-H was observed as a multiplet in the case of **5**, while it was observed as a doublet in the case of **1** ($J_{3''H,4''H}$=10 Hz) and **2** ($J_{3''H,4''H}$=12 Hz). Further, based on molecular models (Dreiding models), it was concluded that the dihedral angle between $C_{2''}$-H and $C_{3''}$-H in **1** or **2** was approximately a right angle. On the other hand, the signal of $C_{3''}$-H in **5** was observed as a complicated pattern, suggesting that the dihedral angle between $C_{2''}$-H and $C_{3''}$-H was not a right angle. This suggests that **5** might be a C-4″ epimer (*cis*-isomer) of **2**.

The structure of isolinderatone was confirmed as follows (Chart 2). We have already reported[2] that hydrogenolysis of **2** with Raney Ni (W-3) in ethanol gave **1** as a sole product, which could be transformed into cyclolinderatin (**6**) by acid treatment. On the other hand, isolinderatone (**5**), the C-4″ epimer (*cis*-isomer) of **2**, can also be easily converted into the corresponding benzopyrandihydrochalcone **13** (C-4″ epimer of **6**), which can be derived from the readily available rubranine (**7**).[8]

Thus, catalytic reduction of **7** with 10% Pd–C in ethyl acetate gave the dihydrochalcone **8**, which was subjected to selective cleavage[8] of a pyran ring with acetic anhydride, affording an isopropenyl derivative **9** as a sole product. In the ^{1}H-NMR spectrum of **9**, signals of a methyl group on a double bond (δ 1.88), an *exo*-methylene group (δ 4.25 and 4.59, d×2), and an acetyl group (δ 2.13) were observed instead of those of geminal methyl groups (δ 1.08 and 1.55 in **8**). This suggests that the resulting product has an isopropenyl group and an acetyl group, and the structure of

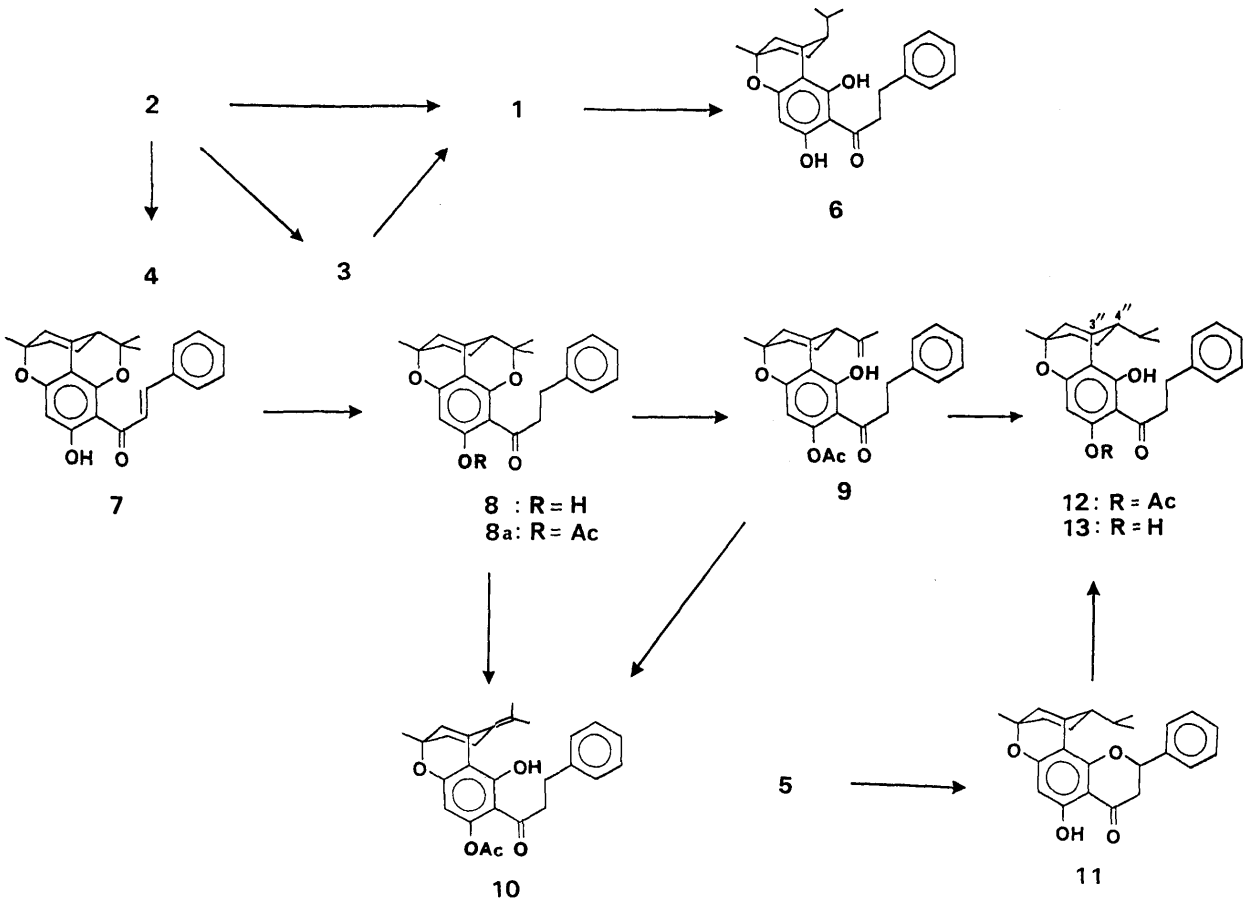

Chart 2

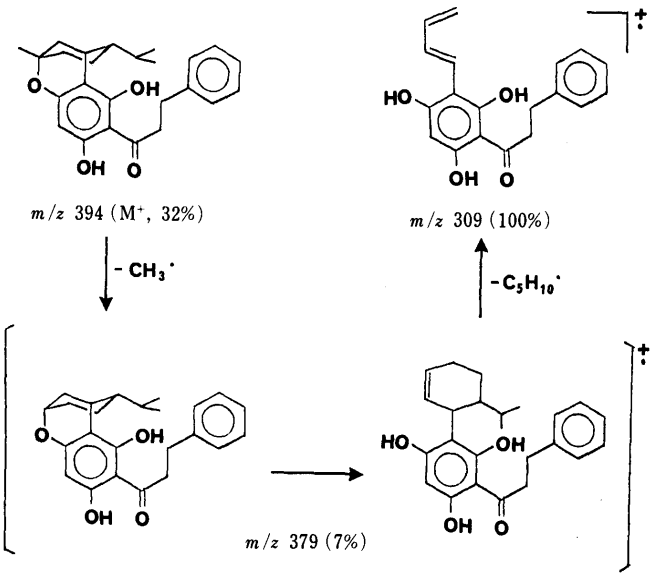

Chart 3

this compound was concluded to be **9**. To elucidate the position of the acetoxyl group in **9**, the following reactions were carried out. Acetylation of **8**, followed by cleavage of the resulting acetate **8a** with *p*-toluenesulfonic acid in benzene, gave an isopropylidene-dihydrochalcone **10** in quantitative yield. Isomerization of **9** with *p*-toluenesulfonic acid in benzene also afforded an isopropylidene derivative which was identical with **10** derived from **8a**. Hydrogenation of **9** with Adam's catalyst in ethanol provided an isopropyl derivative **12**, which, on subsequent hydrolysis, was transformed into the benzopyrandihydrochalcone **13** (C-4″ epimer of **6**). The MS of **13**, as in the cases of other benzopyran derivatives (**6** and **11**),[9] showed a characteristic peak at *m/z* 309 ($M^+ - 15 - 70$) which was formed by demethylation and subsequent retro Diels–Alder reaction of the resulting 4-isopropylcyclohexene group (Chart 3). Next, treatment of **5** with boron trifluoride etherate in chloroform gave a benzopyran derivative **11**.[10] Hydrogenolysis of **11** with Raney Ni (W-3) in ethanol provided a dihydrochalcone derivative which was identical not with **6** but with the product **13** derived from rubranine (**7**).

Therefore, the structure of isolinderatone must be represented by the formula **5**. It is particularly interesting that we could obtain the two epimers, linderatone (**2**) and isolinderatone (**5**), from the same natural source.

Experimental

All melting points are uncorrected. Optical rotations were measured with a JASCO DIP-181 automatic polarimeter. UV spectra were measured on a JASCO UVIDEC-410 spectrometer, and CD spectra on a JASCO J-20 spectropolarimeter. IR spectra were recorded on a JASCO A-3 spectrometer. MS were obtained on a Hitachi M-52 and high-resolution MS on a M-80 instrument. ^{1}H-NMR spectra were taken with a JEOL PS-100 (100 MHz) and GX-270 (270 MHz), and ^{13}C-NMR spectra with a FX-100 (25.0 MHz) spectrometer. Chemical shifts are expressed in δ (ppm) values with tetramethylsilane as an internal standard. Column chromatographies were run on Merck silica gel 60 (70—230 mesh). Thin-layer chromatography (TLC) was performed on glass plates precoated with Kieselgel 60 F_{254} (Merck).

Extraction and Separation of Compounds The fresh leaves (6.6 kg) of *Lindera umbellata* THUNB. var. *membranacea* (MAXIM.) MOMIYAMA, collected in Gifu prefecture in July 1985, were extracted with MeOH. The MeOH extract was divided into the *n*-hexane-soluble (86 g) and $CHCl_3$-soluble (290 g) fractions. A portion of the *n*-hexane-soluble fraction (56 g) was chromatographed on Florisil. Elution with benzene gave linderatone (**2**, 26 mg) and pinostrobin (35 mg). Further elution with benzene–$CHCl_3$ (10 : 1) gave 5,6-dehydrokawain[11] (16 mg). Another portion of this fraction (8.2 g) was chromatographed on a column of Florisil (*n*-hexane–ether, 5 : 1) and subsequently repeated preparative TLC afforded linderachalcone (**3**, 35 mg). The $CHCl_3$-soluble fraction was chromatographed on Florisil with benzene as an eluent to afford **2** (110 mg), pinostrobin (12 mg), pinocembrin (1508 mg), methyllinderatone (**4**, 34 mg), and isolinderatone (**5**, 45 mg).

Methyllinderatone (4) Viscous oil. $[\alpha]_D$ +68.6° ($CHCl_3$, c=0.35). UV λ_{max}^{MeOH} nm: 232 (sh), 292, 341; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 315, 354. CD (c=0.012, MeOH) [θ] (nm): −6300 (289). MS *m/z*: 406 (M^+), 363, 336, 321. High-resolution MS *m/z* Calcd for $C_{26}H_{30}O_4$ (M^+): 406.2142. Found: 406.2158; Calcd for $C_{21}H_{20}O_4$: 336.1361. Found: 336.1368. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 1630, 1570, 1495. ^{1}H-NMR ($CDCl_3$) δ: 0.79, 0.84 (6H, d×2, J=7 Hz, 2×8″-Me), 1.66 (3H, brs, 1″-Me), 2.76 (1H, dd, J=4, 17 Hz, 3β-H), 3.10 (dd, J=13, 17 Hz, 3α-H), 3.77 (3H, s, OMe), 5.16 (1H, brs, 2″-H), 5.43 (1H, dd, J=4, 13 Hz, 2-H), 6.08 (1H, s, 6-H), 7.44 (5H, s, Ar-H), 12.34 (1H, s, OH). ^{13}C-NMR: Table I.

Isolinderatone (5) Viscous oil. $[\alpha]_D$ −67.1° (c=1.25, $CHCl_3$). UV λ_{max}^{MeOH} nm: 222, 294, 325; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 218 (sh), 315, 384. CD (c=0.333, MeOH) [θ] (nm): −9400 (288). MS *m/z*: 392 (M^+), 349, 322, 307. High-resolution MS *m/z* Calcd for $C_{25}H_{28}O_4$ (M^+): 392.1986. Found: 392.1975; Calcd for $C_{20}H_{18}O_4$: 322.1203. Found: 322.1193. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3370, 1640, 1600, 1445. ^{1}H-NMR ($CDCl_3$) δ: 0.55, 0.79 (6H, d×2, J=7 Hz, 2×8″-Me), 1.77 (3H, brs, 1″-Me), 2.75 (1H, dd, J=4, 17 Hz, 3β-H), 3.07 (1H, dd, J=13, 17 Hz, 3α-H), 3.66—3.92 (1H, m, 3″-H), 5.30 (1H, dd, J=4, 13 Hz, 2-H), 5.50 (1H, brs, 2″-H), 6.04 (1H, s, 6-H), 7.39 (5H, s, Ar-H), 12.34 (1H, s, 5-OH). ^{13}C-NMR: Table I.

Methylation of 2 with CH_2N_2 A solution of **2** (20 mg) in CH_2N_2–ether (5 ml) was stirred at room temperature for 5 h and then concentrated *in vacuo*. The residue was purified by preparative TLC ($CHCl_3$–acetone, 20 : 1) to afford a viscous oil (11 mg, 53%). $[\alpha]_D$ +51.1° (c=0.36, $CHCl_3$). High-resolution MS *m/z* Calcd for $C_{26}H_{30}O_4$ (M^+): 406.2142. Found: 406.2093; Calcd for $C_{21}H_{20}O_4$: 336.1361. Found: 336.1389. This compound was identical with **4** by direct comparison (IR, ^{1}H-NMR, MS, co-TLC in a variety of solvent systems).

Hydrogenation of Rubranine (7) A mixture of **7** (1.3 g) and 10% Pd–C (0.6 g) in AcOEt (50 ml) was stirred at room temperature under a hydrogen atmosphere until the absorption of hydrogen ceased. The reaction mixture was filtered and the filtrate was evaporated to dryness. Recrystallization of the residue from EtOH afforded **8** as colorless prisms (1.3 g, quantitative yield). mp 136—138 °C. UV λ_{max}^{MeOH} nm: 233, 293. MS *m/z*: 392 (M^+), 377, 309. High-resolution MS *m/z* Calcd for $C_{25}H_{28}O_4$ (M^+): 392.1985. Found: 392.1979; Calcd for $C_{19}H_{17}O_4$: 309.1125. Found: 309.1082. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620, 1590, 1480. ^{1}H-NMR ($CDCl_3$) δ: 1.08, 1.55 (6H, s×2, 2×8″-Me), 1.37 (3H, s, 1″-Me), 2.88—3.56 (4H, m, α- and β-H), 5.98 (1H, s, 5′-H), 7.18 (5H, s, Ar-H), 13.37 (1H, brs, OH).

Treatment of 8 with Ac_2O A mixture of **8** (1.3 g) and Ac_2O (25 ml) in AcOH (25 ml) was heated under reflux for 3 h. After cooling, the reaction mixture was poured into ice-water, and the mixture was neutralized by addition of $NaHCO_3$ powder under vigorous stirring, then the precipitated solid was collected by filtration. The solid was recrystallized from cyclohexane to afford **9** as colorless prisms (1.24 g, 86%). mp 153—155 °C. UV λ_{max}^{MeOH} nm: 222, 291. MS *m/z*: 434 (M^+), 392, 351, 309. High-resolution MS *m/z* Calcd for $C_{27}H_{30}O_5$ (M^+): 434.2092. Found: 434.2092; Calcd for $C_{19}H_{17}O_4$: 309.1125. Found: 309.1092. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1765, 1620, 1580. ^{1}H-NMR ($CDCl_3$) δ: 1.36 (3H, s, 1″-Me), 1.88 (3H, s, 8″-Me), 2.13 (3H, s, COMe), 2.86—3.28 (4H, m, α- and β-H), 4.25, 4.59 (2H, d×2, J=2 Hz, 9″-H), 6.05 (1H, s, 5′-H), 7.16—7.24 (5H, m, Ar-H), 13.53 (1H, s, OH).

Acetylation of 8 A solution of **8** (20 mg) in Ac_2O (0.5 ml) and pyridine (0.5 ml) was stirred at room temperature overnight. The reaction mixture was poured into ice-water and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried over Na_2SO_4, and evaporated to dryness to give **8a** as colorless needles (20 mg, 90%). mp 106—108 °C. UV λ_{max}^{MeOH} nm: 227, 278. MS *m/z*: 434 (M^+), 392, 351, 309. High-resolution MS *m/z* Calcd for $C_{27}H_{30}O_5$ (M^+): 434.2092. Found: 434.2092; Calcd for $C_{19}H_{17}O_4$: 309.1125. Found: 309.1161. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1760, 1670, 1605, 1480. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 0.95, 1.52 (6H, s×2, 2×8″-Me), 1.38 (3H, s, 1″-Me), 2.23 (3H, s, COMe), 2.98 (2H, t, J=6.7 Hz, β-H), 3.13—3.37 (2H, m, α-H), 6.23 (1H, s, 5′-H), 7.14—7.36 (5H, m, Ar-H).

Treatment of 8a with *p*-TsOH A mixture of **8a** (7 mg) and *p*-TsOH (10 mg) in dry benzene (1 ml) was refluxed for 4 h. After cooling, a small

amount of $CHCl_3$ was added to the reaction mixture. Then the mixture was washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was purified on a silica gel column ($CHCl_3$) to afford **10** as a viscous oil (7 mg, quantitative yield). UV λ_{max}^{MeOH} nm: 290. MS *m/z*: 434 (M^+), 392, 309. High-resolution MS *m/z* Calcd for $C_{27}H_{30}O_5$ (M^+): 434.2092. Found: 434.2087; Calcd for $C_{19}H_{17}O_4$: 309.1125. Found: 309.1126. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610, 1765, 1620, 1605. ^{1}H-NMR (270 MHz, $CDCl_3$) δ: 1.36 (3H, s, 1″-Me), 1.66 (3H, s, 8″-Me), 1.93 (3H, d, J= 1.7 Hz, 8″-Me), 2.17 (3H, s, COMe), 2.95—3.02 (2H, m, β-H), 3.13—3.20 (2H, m, α-H), 4.33 (1H, br s, 3″-H), 6.07 (1H, s, 5′-H), 7.19—7.29 (5H, m, Ar-H), 13.65 (1H, s, OH).

Treatment of 9 with *p*-TsOH A mixture of **9** (10 mg) and *p*-TsOH (10 mg) in dry benzene (1 ml) was refluxed for 2 h. After cooling, a small amount of $CHCl_3$ was added to the reaction mixture. Then the mixture was washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was purified on a silica gel column ($CHCl_3$) to afford a viscous oil (10 mg, quantitative yield). High-resolution MS *m/z* Calcd for $C_{27}H_{30}O_5$ (M^+): 434.2092. Found: 434.2120; Calcd for $C_{19}H_{17}O_4$: 309.1125. Found: 309.1149. This compound was identical with **10** derived from **8a** by direct comparison (IR, ^{1}H-NMR, MS, co-TLC in a variety of solvent systems).

Hydrogenation of 9 A mixture of **9** (200 mg) and PtO_2 (50 mg) in EtOH (15 ml) was stirred at room temperature under a hydrogen atmosphere until the absorption of hydrogen ceased. The reaction mixture was filtered and the filtrate was evaporated to give **12** as a viscous oil (200 mg, quantitative yield). UV λ_{max}^{MeOH} nm: 291. MS *m/z*: 436 (M^+), 394, 309. High-resolution MS *m/z* Calcd for $C_{27}H_{32}O_5$ (M^+): 436.2248. Found: 436.2282; Calcd for $C_{19}H_{17}O_4$: 309.1125. Found: 309.1103. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1765, 1615, 1580, ^{1}H-NMR ($CDCl_3$) δ: 0.75, 1.14 (6H, d × 2, J=6 Hz, 2 × 8″-Me), 1.33 (3H, s, 1″-Me), 2.13 (3H, s, COMe), 2.91—3.27 (4H, m, α- and β-H), 5.99 (1H, s, 5′-H), 7.12—7.20 (5H, m, Ar-H), 13.80 (1H, s, OH).

Hydrolysis of 12 A solution of **12** (18 mg) in 1 N KOH–EtOH (2 ml) was refluxed under a nitrogen atmosphere for 10 min. After cooling, the reaction mixture was acidified with dilute HCl and extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried over Na_2SO_4, and then evaporated to dryness. The residue was purified by preparative TLC (*n*-hexane–acetone, 5 : 1) to give **13** as a viscous oil (14 mg, 86%). UV λ_{max}^{MeOH} nm: 228(sh), 294. MS *m/z*: 394 (M^+), 379, 309. High-resolution MS *m/z* Calcd for $C_{25}H_{30}O_4$ (M^+): 394.2142. Found: 394.2145; Calcd for $C_{19}H_{17}O_4$: 309.1125. Found: 309.1079. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 3250, 1620, 1590. ^{1}H-NMR ($CDCl_3$) δ: 0.76, 1.14 (6H, d × 2, J=6 Hz, 2 × 8″-Me), 1.33 (3H, s, 1″-Me), 2.86—3.48 (4H, m, α- and β-H), 5.66 (1H, s, 5′-H), 7.15 (5H, s, Ar-H), 13.76 (1H, s, OH).

Treatment of 5 with $BF_3 \cdot Et_2O$ $BF_3 \cdot Et_2O$ (1 drop) was added to a solution of **5** (5 mg) in $CHCl_3$ (1 ml), and the mixture was stirred at room temperature. After 15 min, a small amount of ice was added to the reaction mixture and the whole was extracted with $CHCl_3$. The $CHCl_3$ layer was washed with water, dried over Na_2SO_4, and evaporated to dryness. The residue was purified on a silica gel column ($CHCl_3$) to afford **11** as a viscous oil (4 mg, 80%). $[\alpha]_D$ −39.2° (c=0.12, $CHCl_3$). UV λ_{max}^{MeOH} nm: 224, 295, 322(sh). MS *m/z*: 392 (M^+), 377, 307. High-resolution MS *m/z* Calcd for $C_{25}H_{28}O_4$ (M^+): 392.1985. Found: 392.1981; Calcd for $C_{19}H_{15}O_4$: 307.0968. Found: 307.0937. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1640, 1625, 1585, 1480. ^{1}H-NMR ($CDCl_3$) δ: 0.93, 0.97 (6H, d × 2, J=7 Hz, 2 × 8″-Me), 1.37 (3H, s, 1″-Me), 2.84—3.20 (2H, m, 3-H), 3.28—3.44 (1H, m, 3″-H), 5.44 (1H, dd, J=5, 12 Hz, 2-H), 5.92 (1H, s, 6-H), 7.33 (5H, s, Ar-H), 11.85 (1H, br s, OH).

Hydrogenolysis of 11 A mixture of **11** (4 mg) and Raney Ni (W-3) in EtOH (1 ml) was stirred at room temperature under a hydrogen atmosphere for 1.5 h. The reaction mixture was filtered and the filtrate was evaporated to dryness. The residue was purified by preparative TLC (*n*-hexane–acetone, 5 : 1) to afford a viscous oil (2 mg, 50%). $[\alpha]_D$ −24.6° (c= 0.13, $CHCl_3$). High-resolution MS *m/z* Calcd for $C_{25}H_{30}O_4$ (M^+): 394.2142. Found: 394.2117; Calcd for $C_{19}H_{17}O_4$: 309.1125. Found: 309.1093. This compound was indistinguishable from **13** derived from rubranine (**7**) by direct comparison (IR, ^{1}H-NMR, MS, co-TLC in a variety of solvent systems).

References and Notes

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9) In the MS of all the other benzopyran derivatives related to linderatin, a characteristic fragmentation peak was observed as the base peak at *m/z* (M^+ − 85) or (M^+ − 83); this fragment was formed by demethylation and subsequent retro Diels–Alder reaction of the resulting 4-isopropyl- or 4-isopropenylcyclohexene group.
10) This compound **11** was not identical with cyclolinderatone[2] derived from linderatone (**2**) by the same procedure.