# Diterpenoid Constituents of *Rabdosia umbrosa* (MAXIM.) HARA: Isolation and Structure Elucidation of Two New Diterpenoids, Umbrosianin and Rabdoumbrosanin

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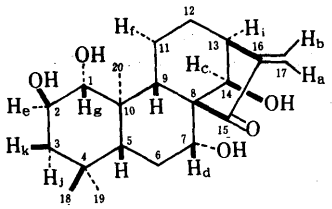
**Diterpenoid constituents of the aerial parts of *Rabdosia umbrosa* (MAXIM.) HARA, collected in Gotenba City and Shizuoka City were separately examined. A new compound, umbrosianin (1), has been isolated together with two known compounds, umbrosin A (2) and kamebanin (3), from the former and a new compound, rabdoumbrosanin (6) has been isolated together with four known compounds, shikoccidin (4), isodomedin (5), shikoccin (7) and rabdolatifolin (8), from the latter. The structures of the new compounds have been elucidated on the basis of spectral and chemical evidence.**

**Keywords** *Rabdosia umbrosa*; Labiatae; umbrosianin; *ent*-kaurenoid; rabdoumbrosanin; 8,9-*seco*-*ent*-kaurenoid; structure elucidation

From the plants of the genus *Rabdosia* (Labiatae), over one hundred diterpenoids having *ent*-kaurene, 6,7-*seco*-*ent*-kaurene, 8,9-*seco*-*ent*-kaurene, 7,20-*cyclo*-*ent*-kaurene and *ent*-gibberellane skeletons have been isolated and characterized.[2)] Among them, umbrosins A (**2**) and B (2-dehydro derivative of **2**) were isolated from *R. umbrosa* (MAXIM.) HARA.[3)] During the course of our studies on the biologically active substances from the genus *Rabdosia*, we separately examined the diterpenoid constituents of the aerial parts of the title plant collected in Gotenba City and Shizuoka City (Japan). A new diterpenoid, named umbrosianin (**1**), was isolated together with two known compounds, umbrosin A (**2**)[3)] and kamebanin (**3**)[4)] from the former. On the other hand, a new diterpenoid, named rabdoumbrosanin (**6**), was isolated together with four known compounds, **3**, shikoccidin (**4**),[5)] isodomedin (**5**),[6)] shikoccin (**7**)[5)] and rabdolatifolin (**8**)[7)] from the latter. This paper deals with the structure elucidation of the new compounds.

Umbrosianin (**1**), mp 180—182 °C, $[\alpha]_D$ −81.5 ° (MeOH), was determined to have the molecular formula, $C_{20}H_{30}O_5$, on the basis of its high resolution mass spectrum (high-MS). Umbrosianin (**1**) showed an absorption maximum at 231 nm (ε 6848) in the ultraviolet (UV) spectrum, absorption bands at 1730 and 1650 $cm^{-1}$ in the infrared (IR) spectrum, signals at δ 5.36 and 6.31 (each 1H, br s, $H_b$ and $H_a$) in the proton nuclear magnetic resonance ($^1$H-NMR) spectrum ($C_5D_5N$) and signals at δ 115.5(t) (*exo*-methylene) and 208.4 (ketone) in the carbon-13 nuclear magnetic resonance ($^{13}$C-NMR) spectrum ($C_5D_5N$, Table I). From these spectral data, **1** was suggested to contain a five membered ketone conjugated with an *exo*-methylene group as a partial structure, which is very common among the diterpenoids isolated from the genus *Rabdosia*.[2)] In addition to three tertiary methyl groups ($\delta_H$ 0.87, 0.92 and 1.46), umbrosianin (**1**) was suggested to contain four secondary carbinyl functional groups (hydroxyl groups) from the inspection of the $^1$H-NMR [δ 5.27 (1H, br s, $H_c$), 4.76 (1H, dd, $J$=11.5, 4.5 Hz, $H_d$), 4.08 (1H, ddd, $J$=12, 9, 4.5 Hz, $H_e$), and 3.34 (1H, d, $J$=9 Hz, $H_g$)] and $^{13}$C-NMR (δ 69.0, 74.4, 75.8, 85.8) spectra. The $^{13}$C-NMR spectrum of **1** further showed signals due to three methyl groups, four methylene groups, three methine groups and three quaternary carbon atoms. The above mentioned spectral data suggested that umbrosianin (**1**) is tetracyclic and has an *ent*-kaur-16-en-15-one structure as a basic skeleton. The confirmation of the partial structure around the D-ring and the determination of the locations of the four hydroxyl groups were achieved by spin–spin decoupling and nuclear Overhauser enhancement (NOE) experiments in the $^1$H-NMR spectra. On irradiations at the frequencies of $H_a$, $H_b$ and $H_c$, the signal of $H_b$, those of $H_a$ and $H_i$ (δ 3.31, m, 13-H), and that of $H_i$ were sharpened, respectively. When the frequency of $H_i$ was irradiated, the signals of $H_a$, $H_b$ and $H_c$ were sharpened. These results confirmed not only the structure around the D-ring, but also the location of one hydroxyl group at C-14β. On irradiation at the frequency of $H_e$, the signals of $H_g$, $H_j$ (δ 1.87, dd, $J$=12, 4.5 Hz) and $H_k$ (δ 1.56, dd, $J$=12, 12 Hz) changed to a singlet, a doublet ($J$=12 Hz) and a doublet ($J$=12 Hz), respectively. On the other hand, the signal of $H_e$ collapsed to a double doublet ($J$=12, 4.5 Hz) and a double doublet ($J$=12, 9 Hz) on irradiations at the frequencies of $H_g$ and $H_j$, respectively. The results supported the presence of the partial structure (**10**) in **1**. The signal (δ 3.68, 1H, m; $H_f$) assignable to 11α-H showed an abnormal downfield shift. This phenomenon could be well explained by an α-equatorial hydroxyl group located at C-1, and was observed in the case of kamebanin (**3**) (δ 3.2).[4)] Accordingly, two hydroxyl groups should be located at C-1α and C-2β. These assignments were supported by the results of NOE experiments. On irradiation at δ 1.46 (20-$H_3$), NOE's were observed for $H_c$ (17%) and $H_e$ (12%), respectively. The remaining hydroxyl group was presumed to be located at C-7α on the basis that 7β-axial hydrogen ($H_d$) might suffer an anisotropic effect from the carbonyl group at C-15 and consequently show a downfield shift. This presumption was shown to be correct by the formation of the diacetonide (**12**) [$\delta_H$ ($CDCl_3$) 1.19, 1.24, 1.33, 1.38 (each 3H, s, 4 × acetonide Me) when **1** was treated with 2,2-dimethoxypropane in the presence of *p*-toluenesulfonic acid in *N*,*N*-dimethylformamide (DMF). Accordingly, the structure of umbrosianin was elucidated as **1** except for the absolute stereochemistry. The absolute stereochemistry was determined from the fact that the dihydro compound (**11**) obtained by catalytic hydrogenation showed a negative Cotton effect in the optical rotatory dispersion (ORD) spectrum.[8)] On the basis of these results, the structure of umbrosianin was elucidated as **1**.



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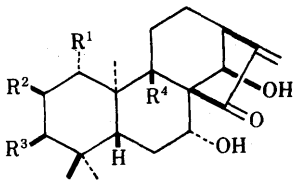
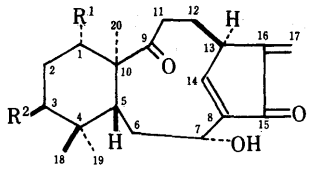
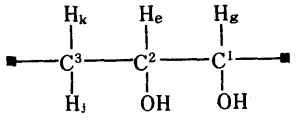


2 : $R^1=R^3=R^4=H$; $R^2=OH$
3 : $R^1=OH$, $R^2=R^3=R^4=H$
4 : $R^1=R^2=H$; $R^3=OAc$, $R^4=OH$
5 : $R^1=OH$, $R^2=R^4=H$, $R^3=OAc$



6 : $R^1=R^2=H$
7 : $R^1=H$, $R^2=OAc$
8 : $R^1=OH$, $R^2=H$
9 : $R^1=R^2=OAc$



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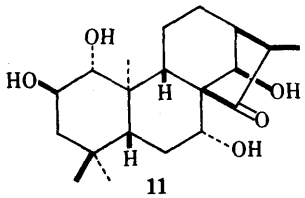

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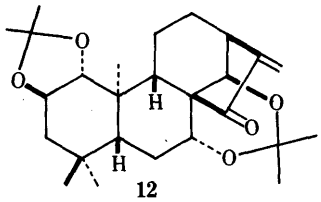

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Rabdoumbrosanin (**6**) was obtained as a colorless syrup, $[\alpha]_D$ −40.6° (MeOH) and the molecular formula was determined as $C_{20}H_{28}O_3$ by high-MS. It showed an absorption maximum at 242 nm (ε 4049) in the UV spectrum and absorptions at 3400, 1700, 1650 and 1620 $cm^{-1}$ in the IR spectrum. Besides the signals due to three tertiary methyl groups (δ 0.95, 0.97, 1.03), the $^1$H-NMR spectrum ($CDCl_3$) of **6** showed the presence of one secondary carbinyl proton (δ 4.71, dd, $J$=12, 5 Hz), an *exo*-methylene group (δ 5.46, 6.15) and a trisubstituted double bond (δ 7.26, d, $J$=2 Hz) conjugated with a carbonyl group. The $^{13}$C-NMR spectrum ($CDCl_3$, Table I) showed signals due to two ketone groups, an *exo*-methylene group, a trisubstituted double bond, and one secondary carbinyl carbon atom, together with signals due to three methyl groups, six methylene groups, two methine groups and two quaternary carbon atoms. These spectral data suggested that rabdoumbrosanin (**6**) has a tricarbocyclic 8,9-*seco*-*ent*-kaurene skeleton, and are very similar to those of rabdolatifolin (**8**)[7] except for the numbers of secondary carbinyl carbon atoms and methylene groups. Namely, the number of secondary carbinyl carbon atoms is reduced from two to one and that of methylene groups is increased from five to six in **1** compared to those of **8**. The location of the sole hydroxyl group was assigned to C-7 from comparisons of the $^{13}$C-NMR spectra of **6**, **7**, **8** and shikodomedin (**9**).[9] Namely, in the $^{13}$C-NMR spectrum of **6**, the signal due to the secondary carbinyl carbon (δ 64.4) resonated in almost the same region as the C-7 signals of **7** (δ 64.1, $CDCl_3$), **8** (δ 64.0, $C_5D_5N$), and **9** (δ 63.8, $CDCl_3$). The configuration was elucidated as α on the basis of the comparison of the coupling constant ($J$=12, 5 Hz) with those of the corresponding proton in **7** ($J$=12, 5 Hz), **8** ($J$=12, 7 Hz) and **9** ($J$=12, 6 Hz). From these data, the structure of rabdoumbrosanin could be represented as **6**, which corresponds to 1-deoxyrabdolatifolin. This was further supported by comparisons of the $^{13}$C-NMR spectra of **6** and **8**. The signal due to C-10 in **6** resonated *ca.* 6 ppm upfield compared to that in **8**. The absolute stereochemistry was established from the fact that **6** showed essentially the same Cotton effect [$\lambda_{max}^{MeOH}$ nm (φ): 400 (−375), 384 (−474), 339 (+474)] as that of **8**.[7]

The structure of umbrosianin has a novel oxidation pattern in which both C-1 and C-2 are hydroxylated, and that of rabdoumbrosanin might be the most basic structure in the 8,9-*seco*-*ent*-kaurene series diterpenoids.

TABLE I. Carbon-13 Chemical Shifts (δ) of Umbrosianin (**1**) and Rabdoumbrosanin (**6**)

| Carbon | 1[a] | 6[b] |
|---|---|---|
| 1 | 85.8 | 34.1 |
| 2 | 69.0 | 18.1 |
| 3 | 48.5 | 41.4 |
| 4 | 34.0 | 34.6 |
| 5 | 52.3 | 43.5 |
| 6 | 29.5 | 36.7 |
| 7 | 74.4 | 64.4 |
| 8 | 62.5 | 146.0 |
| 9 | 56.4 | 215.1 |
| 10 | 45.8 | 53.8 |
| 11 | 20.2 | 30.7 |
| 12 | 31.8 | 25.8 |
| 13 | 47.3 | 42.4 |
| 14 | 75.8 | 159.5 |
| 15 | 208.4 | 195.0 |
| 16 | [c] | 148.4 |
| 17 | 115.5 | 116.7 |
| 18 | 33.5 | 33.6 |
| 19 | 22.4 | 22.3 |
| 20 | 16.4 | 16.6 |

*a*) Measured in $C_5D_5N$ solution. *b*) Measured in $CDCl_3$ solution. *c*) The signal of this carbon overlapped with the solvent signal.

**Experimental**

Melting points were determined with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were recorded with a Hitachi 215 spectrophotometer. $^1$H- (200 MHz) and $^{13}$C- (50 MHz) NMR spectra were obtained on a JEOL JNM FX-200 instrument. Chemical shifts are given in δ (ppm) values using tetramethylsilane as an internal standard. UV spectra were taken with a Hitachi 330 spectrophotometer. Optical rotation and optical rotatory dispersion spectra were taken on a spectrometer, JASCO model ORD/UV-5. Mass spectra were determined with a JEOL JMS D-300 spectrometer. Kieselgel 60 (0.05—0.2 mm; Merck) was used for column chromatography and precoated silica gel plates $F_{254}$ (0.25 and 0.5 mm in thickness) were used for thin layer chromatography (TLC). Extracts were dried over anhydrous $MgSO_4$.

**Isolation of Umbrosianin (1)** Dried aerial parts (2.4 kg) of *R. umbrosa* collected in Gotenba City in early October, 1980, were extracted with MeOH (54 l) at room temperature for 1 week. The plant material was extracted again with an equal amount of MeOH for 2 weeks. The combined methanolic extracts were concentrated *in vacuo* and the residue was dissolved in 90% MeOH (1.5 l). After being washed with *n*-hexane (1 l×3), the 90% MeOH layer was concentrated *in vacuo*. The residue was suspended in $H_2O$ (1 l) and the suspension was extracted with EtOAc (1 l×3). The dried EtOAc extract was evaporated *in vacuo* to give a residue (50 g) which was chromatographed on silica gel (1.5 kg). The column was eluted first with $CHCl_3$ (8.5 l), and then successively with $CHCl_3$–$Me_2CO$ (19:1) (10 l), $CHCl_3$–$Me_2CO$ (9:1) (8 l), $CHCl_3$–$Me_2CO$ (17:3) (10.5 l) $CHCl_3$–$Me_2CO$ (4:1) (5 l) and $CHCl_3$–$Me_2CO$ (7:3) (8.5 l), collecting

500 ml fractions.

Fractions 46—58 were combined and the solvent was removed *in vacuo*. The residue (5.18 g) was chromatographed on a silica gel (300 g) column with $Et_2O$, collecting 50 ml fractions. Fractions 18—25 were combined and evaporated *in vacuo* to give a residue (1.45 g), a portion (60 mg) of which was repeatedly purified by preparative TLC (solvent: $CHCl_3$–$Me_2CO$ (17 : 3) and $Et_2O$) to give kamebanin (**3**) (7 mg).

Fractions 64—71 were combined and evaporated *in vacuo* to give a residue (3.02 g). After being washed with $CHCl_3$, the residue was recrystallized from MeOH to give umbrosin A (**2**) (974 mg).

Fractions 85—95 were combined and evaporated *in vacuo*. The residue (1.85 g) was subjected to silica gel (150 g) column chromatography. Elution was carried out first with $CHCl_3$ (900 ml), and successively with $CHCl_3$–MeOH (97 : 3) (600 ml), $CHCl_3$–MeOH (24 : 1) (300 ml) and $CHCl_3$–MeOH (19 : 1) (750 ml), collecting 75 ml fractions. Fractions 23—28 gave a residue (374 mg), which was repeatedly purified by silica gel (60 g) column chromatography with $CHCl_3$–MeOH as the eluant, preparative TLC (solvent: $CHCl_3$–MeOH (9 : 1), developed three times) and finally recrystallization from MeOH to give umbrosianin (**1**) (70.6 mg) as colorless needles, mp 180—182 °C.

Kamebanin (**3**) was identified by comparison with an authentic sample on the basis of mixed melting point determination and comparisons of the IR and $^1$H-NMR spectra. Umbrosin A (**2**) was identified on the basis of comparisons of the spectral data of its triacetate with the reported data.[3]

Umbrosianin (**1**): $[\alpha]_D^{22}$ −81.5° ($c$=0.18, MeOH). UV $\lambda_{max}^{MeOH}$ nm ($\varepsilon$): 231 (6848). IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3700—3050, 1730, 1650. $^1$H-NMR ($C_5D_5N$) $\delta$: 0.87 and 0.92 (each 3H, s, 18- and 19-$H_3$), 1.46 (3H, s, 20-$H_3$), 1.56 (1H, dd, $J$=12, 12 Hz, 3$\beta$-H; $H_k$), 1.87 (1H, dd, $J$=12, 4.5 Hz, 3$\alpha$-H; $H_j$), 3.31 (1H, m, 13-H; $H_i$), 3.34 (1H, d, $J$=9 Hz, 1-H; $H_g$), 3.68 (1H, m, 11$\alpha$-H; $H_f$), 4.08 (1H, ddd, $J$=12, 9, 4.5 Hz, 2-H; $H_e$), 4.76 (1H, dd, $J$=11.5, 4.5 Hz, 7-H; $H_d$), 5.27 (1H, br s, 14-H; $H_c$), 5.36 and 6.31 (each 1H, br s, 17-$H_2$; $H_b$ and $H_a$), and 7.43 and 8.13 (each 1H, m, OH). $^{13}$C-NMR: see Table I. MS $m/z$: 350.2091 $(M)^+$. Calcd for $C_{20}H_{30}O_5$: 350.2093.

**Umbrosianin Diacetonide (12)** 2,2-Dimethoxypropane (1 ml) and $p$-toluenesulfonic acid (1 mg) were added to a solution of umbrosianin (**1**) (10.6 mg) in DMF (1 ml) and the mixture was heated at 80 °C for 3 h. The solvent was removed *in vacuo* to give a residue, which was dissolved in $CHCl_3$ (30 ml), and the solution was washed successively with 5% aqueous $NaHCO_3$ (30 ml) and saturated aqueous NaCl (30 ml × 2), then dried and evaporated *in vacuo*. The residue was purified on a silica gel plate (solvent: $CHCl_3$–$Me_2CO$ (19 : 1)) to give the diacetonide (**12**) (8.5 mg) as an amorphous powder. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 2980, 2930, 2860, 1730, 1645, 1460, 1380, 1370, 1240, 1160, 1105, 1065, 935, 855. $^1$H-NMR ($CDCl_3$) $\delta$: 0.93 and 1.00 (each 3H, s, 4-$Me_2$), 1.19, 1.24, 1.33, and 1.38 (each 3H, s, acetonide $Me_4$), 1.58 (3H, s, 10-Me), 2.87 (1H, d, $J$=9 Hz, 1-H), 3.04 (1H, m, 13-H), 3.70 (1H, ddd, $J$=12.5, 9, 4 Hz, 2-H), 4.17 (1H, dd, $J$=10, 8 Hz, 7-H), 4.60 (1H, d, $J$=2 Hz, 14-H), 5.38 (1H, br s, 17-$H_1$), 6.15 (1H, br s, 17-$H_1$). FAB-MS $m/z$: 453 $(M+Na)^+$ (+NaI), 469 $(M+K)^+$ (+KI). EI-MS $m/z$: 372.2293 $(M-Me_2CO)^+$. Calcd for $C_{23}H_{32}O_4$: 372.2302.

**Dihydroumbrosianin (11)** Palladium–carbon (5%) (10 mg) was added to a solution of umbrosianin (**1**) (6.7 mg) in MeOH (5 ml) and the mixture was stirred for 3 h in an atmosphere of hydrogen. The catalyst was filtered off and the filtrate was evaporated *in vacuo* to give a residue (5.7 mg) which was purified on a silica gel plate (solvent: $CHCl_3$–MeOH (19 : 1), developed four times) to give the dihydroumbrosianin (**11**) (3.9 mg) as colorless needles, mp 264—267 °C. IR $\nu_{max}^{KBr}$ cm$^{-1}$: 3300 (br), 2920, 2880, 1720, 1460, 1370, 1095, 1050, 925. $^1$H-NMR ($C_5D_5N$) $\delta$: 0.86 and 0.91 (each 3H, s, 4-$Me_2$), 1.19 (3H, d, $J$=7 Hz, 16-Me), 1.46 (3H, s, 10-Me), 2.63 (1H, m, 13-H), 3.23 (1H, m, 16-H), 3.34 (1H, d, $J$=8.5 Hz, 1-H), 3.57 (1H, dd $J$=16, 6 Hz, 11$\alpha$-H), 4.08 (1H, m, 2-H), 4.62 (1H, m, changed to dd on addition of $D_2O$, $J$=11.5, 4.5 Hz, 7-H), 5.35 (1H, br s, 14-H), 5.83 (1H, m, OH), 6.23 (1H, m, OH), 7.31 (1H, br s, OH), 7.86 (1H, d, $J$=5.5 Hz, OH). ORD $\lambda_{max}^{MeOH}$ nm ($\phi$): 322 (−2834), 290 (+564). MS $m/z$: 352.2210. Calcd for $C_{20}H_{32}O_5$: 352.2251.

**Isolation of Rabdoumbrosanin (6)** Dried aerial parts (75 g) of *R. umbrosa* collected in Shizuoka City, Japan, were extracted with MeOH (3 l) at room temperature for 10 d. The methanolic extract was concentrated *in vacuo* to give a residue which was dissolved in 90% MeOH (300 ml). After being washed with *n*-hexane (200 ml × 2), the solution was concentrated *in vacuo*. The residue was suspended in $H_2O$ (200 ml) and extracted with EtOAc (250 ml × 3). The dried EtOAc extract was evaporated *in vacuo* to give a residue (1.56 g), which was chromatographed over silica gel (60 g). Elution was carried out first with $CHCl_3$ (300 ml), and successively with $CHCl_3$–$Me_2CO$ (19 : 1) (500 ml), $CHCl_3$–$Me_2CO$ (9 : 1) (500 ml) and $CHCl_3$–$Me_2CO$ (17 : 3) (500 ml), collecting 50 ml fractions.

Fractions 18—23 were combined and evaporated *in vacuo* to give a residue (53 mg), which was purified on silica gel plates (solvent: $Et_2O$) to give rabdoumbrosanin (**6**) (7.5 mg) as a syrup.

Fractions 24—26 gave a residue (214 mg) on evaporation. The residue was separated by repeated preparative TLC (solvent: $Et_2O$ and $CHCl_3$–$Me_2CO$ (9 : 1)) to give another lot of **6** (3.5 mg) and shikoccin (**7**) (141 mg).

Fractions 28—35 gave a residue (103 mg) which was separated by repeated TLC (solvent: $CHCl_3$–$Me_2CO$ (4 : 1) and $Et_2O$) to give kamebanin (**3**) (25.4 mg) and shikoccidin (**4**) (17.2 mg).

Fractions 40—46 gave a residue (62 mg) which was repeatedly separated by preparative TLC (solvent: $CHCl_3$–$Me_2CO$ (4 : 1)) to give isodomedin (**5**) (20.2 mg) and rabdolatifolin (**8**) (3.6 mg).

Among the isolated compounds, the known compounds (**3**, **4**, **5**, **7**, **8**) were shown to be identical with authentic samples on the basis of comparisons of the spectral data. The data for rabdoumbrosanin (**6**) are as follows.

Rabdoumbrosanin (**6**): A colorless syrup, $[\alpha]_D^{22}$ −40.6° ($c$=0.16, MeOH). UV $\lambda_{max}^{MeOH}$ nm ($\varepsilon$): 242 (4049). IR $\nu_{max}^{CHCl_3}$ cm$^{-1}$: 3400, 1700, 1650, 1620. $^1$H-NMR ($CDCl_3$) $\delta$: 0.95, 0.97 and 1.03 (each 3H, s, 3 × *tert*-Me), 3.62 (1H, m, 13-H), 4.71 (1H, dd, $J$=12, 5 Hz, 7-H), 5.46 and 6.15 (each 1H, br s, 17-$H_2$), 7.26 (1H, d, $J$=2 Hz, 14-H). $^{13}$C-NMR: see Table I. MS $m/z$: 316.2042 $(M)^+$. Calcd for $C_{20}H_{28}O_3$: 316.2038.

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**References and Notes**

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