

Prenylcoumarins from *Murraya paniculata* var. *omphalocarpa* (Rutaceae): The Absolute Configuration of Sibiricin, Mexotycin and Omphamurin

Takeshi KINOSHITA,^{*,a} Jin-Bin WU,^b and Feng-Chi Ho^c

Faculty of Pharmaceutical Sciences, Teikyo University,^a 1091-1 Suarashi, Sagamiko-machi, Kanagawa 199-01, Japan, China Medical College,^b Taichung, Taiwan, Republic of China, and International Institute for Botanical Resources of Tropics,^c Hengchun 946, Taiwan, Republic of China. Received December 8, 1995; accepted February 17, 1996

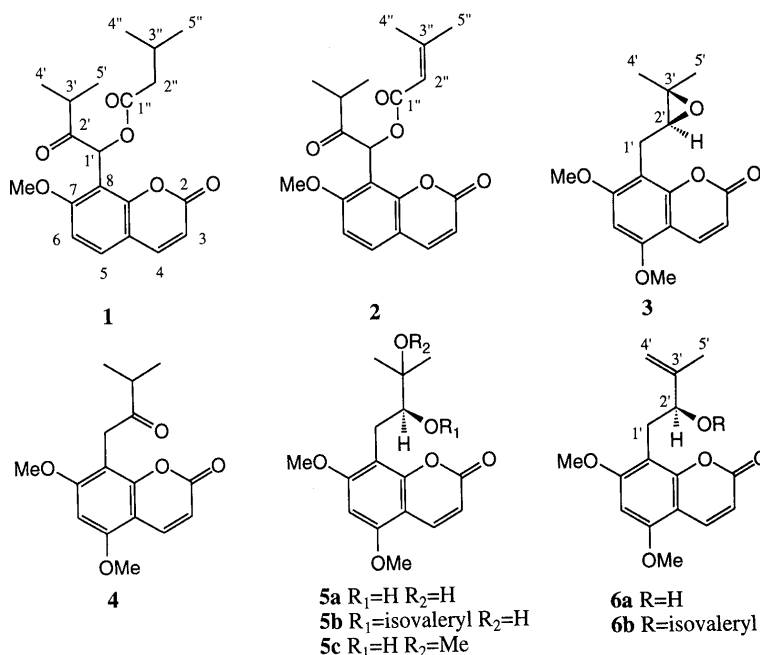
Three new prenylcoumarins, murpaniculol senecioate, 5-methoxymurrayatin and omphamurin isovalerate were isolated from the leaves of *Murraya paniculata* var. *omphalocarpa* (Rutaceae), together with six known coumarins, paniculatin, (–)-sibiricin, 5,7-dimethoxy-8-(3'-methyl-2'-oxobutyl)coumarin, (–)-mexotycin, omphamurin and omphalocarpin. Their structures were characterized on the basis of spectroscopic evidence. The absolute configuration of omphamurin at the C-2' position has been determined to be *S* by Horeau's method. The absolute stereochemistry of (–)-mexotycin and (–)-sibiricin has also been established by their chemical correlation with omphamurin.

Key words *Murraya paniculata* var. *omphalocarpa*; Rutaceae; prenylcoumarin; absolute configuration; ¹³C-NMR assignment

Murraya paniculata var. *omphalocarpa* (HAYATA) TANAKA is a rutaceous shrub indigenous to Lan Yu (Orchid Island), Taiwan, and one of three occurring varieties of *M. paniculata*. This variety is distinguished from the mother species by larger fruits, larger flowers and broad leaflets.¹⁾ Therefore, it is of interest to investigate this variety from a chemosystematic viewpoint since it may indicate a level of chemical differentiation of the variety from the mother species. Previous fragmentary reports revealed the presence of alkaloids, coumarins and flavones in the fruits,²⁾ flowers,³⁾ leaves^{4,5)} and root bark^{6,7)} of this plant. In order to obtain more detailed chemical information on this plant for the above purpose, we have undertaken a chemical investigation of this plant. This report describes the isolation of prenylated coumarins of chemotaxonomic significance, the absolute stereochemistry of (–)-sibiricin (**3**), (–)-mexotycin (**5a**) and omphamurin (**6a**), and the ¹³C assignment of prenylated coumarins.

The acetone extract of the dried leaves of *M. paniculata*

var. *omphalocarpa* was separated by a combination of silica gel, Sephadex LH-20 and reversed-phase silica gel column chromatography to afford compounds **1**–**4**, **5a**–**c** and **6a**, **b**. Compounds **1**, **5c** and **6a** were identified from physical and spectroscopic data by comparison with those reported in the literature as paniculatin,⁵⁾ omphalocarpin,³⁾ and omphamurin,⁴⁾ respectively, which have already been isolated from the same plant by Wu *et al.* Compounds **3**, **4** and **5a** were identified as the known coumarins (–)-sibiricin, 5,7-dimethoxy-8-(3'-methyl-2'-oxobutyl)coumarin and (–)-mexotycin, respectively, by direct comparison with authentic samples previously obtained from *M. paniculata* root bark of Indonesian origin.⁸⁾ Omphalocarpin (**5c**) was described as a natural product in the literature, but it is apparent that this compound is an artifact arising from methanolysis of sibiricin (**3**), since it could not be detected in the original extract but appeared in some chromatographic fractions after being treated with MeOH. Compounds **2**, **5b** and **6b**



* To whom correspondence should be addressed.

were new coumarin derivatives and their structures were elucidated as murpaniculol senecioate, 5-methoxymurrayatin and omphamurin isovalerate, respectively, as mentioned below.

Murpaniculol senecioate (**2**) was obtained as an optically active colorless oil, $[\alpha]_D +123.3^\circ$. The 7-methoxy-8-substituted coumarin skeleton for **2** was indicated by a methoxy signal, and a set of four doublets in the aromatic region of ^1H -nuclear magnetic resonance (^1H -NMR) [δ 3.91 (3H, s), 6.26 (1H, d, $J=9.5$ Hz), 6.88 (1H, d, $J=8.7$ Hz), 7.47 (1H, d, $J=8.7$ Hz) and 7.62 (1H, d, $J=9.5$ Hz)] and ultraviolet (UV) spectra. The side chain at the C-8 position was readily elucidated as $-\text{CH}(\text{OCOR})\text{COCH}(\text{CH}_3)_2$ ($\text{R}=2\text{-methyl-1-butenyl}$) from the ^1H -NMR [δ 1.04, 1.20 (3H each, d, $J=6.7$ Hz), 1.89 (3H, d, $J=1.4$ Hz), 2.19 (3H, d, $J=1.2$ Hz), 2.97 (1H, hept, $J=6.7$ Hz), 5.79 (1H, m) and 7.03 (1H, s)] and ^{13}C -NMR (Table 1) spectra. Thus, it was elucidated as a senecioic acid ester of murpaniculol, a 7-methoxycoumarin isolated from *M. paniculata* leaves.⁹⁾ This compound was chemically prepared from murranganon (murpaniculol) and senecioic acid chloride by Furukawa *et al.*,¹⁰⁾ but this is the first report of isolation from a natural source.

5-Methoxymurrayatin (**5b**) was obtained as an optically active colorless oil, $[\alpha]_D +55.9^\circ$. Its UV and infrared (IR) spectra suggested that this is a 5,7-dimethoxycoumarin derivative. Its ^1H - and ^{13}C -NMR (Table 1) spectra indicated the presence of the same side chain [$-\text{CH}_2\text{CH}(\text{OCOR})\text{C}(\text{OH})(\text{CH}_3)_2$; $\text{R}=(\text{CH}_3)_2\text{CHCH}_2-$] as that of murrayatin, a 7-methoxy-8-prenylcoumarin derivative obtained from *M. exotica*.¹¹⁾ These findings readily assigned the structure of this compound as **5b**. Its optical rotation, IR and ^1H -NMR spectra were in complete agreement with those of a semi-synthetic compound prepared from (–)-mexotycin (**5a**) and isovaleryl chlo-

ride.

Omphamurin isovalerate (**6b**) was obtained as optically active colorless needles, $[\alpha]_D -14.9^\circ$. Its ^1H - and ^{13}C -NMR (Table 1) spectra indicated the presence of an isovaleryl unit, exo-methylene [δ 4.82 and 4.87 (1H each, m)], olefinic methyl [δ 1.85 (3H, s)] and a set of ABC proton signals [δ 3.04 (1H, dd, $J=5.2, 13.7$ Hz), 3.19 (1H, dd, $J=8.6, 13.7$ Hz) and 5.45 (1H, dd, $J=5.2, 8.6$ Hz)]. The structure of this compound was readily elucidated as **6b**, and finally identified with the one prepared from omphamurin (**6a**) and isovaleryl chloride.

Sibiricin (**3**), mexotycin (**5a**) and omphamurin (**6a**) occurred in this plant as their laevorotatory forms. However, the absolute stereochemistry of these coumarins remains unknown. Omphamurin (**6a**) is a secondary alcohol derivative having an asymmetric center at the C-2' position, and thus this secondary alcohol system can be applied to Horeau's empirical rule.¹²⁾ According to this rule, the absolute stereochemistry at the C-2' position of omphamurin (**6a**) was found to be the same *S*-configuration as that of auraptenol, 8-(2'-hydroxy-3'-methyl-3'-butenyl)-7-methoxycoumarin.¹³⁾ The treatment of (–)-sibiricin (**3**) with Lewis acid according to the procedure reported in the literature¹⁴⁾ gave rise to 5,7-dimethoxy-8-(2'-hydroxy-3'-methyl-3'-butenyl)coumarin, though in low yield, which was identical with omphamurin (**6a**), not only chemically but also optically. Since (–)-sibiricin (**3**) has been reported to give rise to (–)-mexotycin (**5a**) on hydrolysis with acid, (–)-sibiricin (**3**), (–)-mexotycin (**5a**) and omphamurin (**6a**) were also correlated chemically and optically. Thus, the absolute configuration of (–)-sibiricin (**3**) and (–)-mexotycin (**5a**) was established as *S* at the C-2' position.

Though ^{13}C -NMR has become an indispensable tool for the structure elucidation of natural products, there has been little information available on ^{13}C resonances

Table 1. ^{13}C -NMR Data for Coumarins Isolated from *Murraya paniculata* var. *omphalocarpa* Leaves

C	1	2	3	4	5a	5b	5c	6a	6b
2	159.7	159.8	161.3	161.2	161.3	161.5 ^{a)}	161.4	161.3 ^{a)}	161.3
3	113.8	113.7	110.9	110.8	110.9	110.2	110.8	110.9	110.7
4	143.2	143.2	138.7	138.8	138.9	139.0	138.8	138.8	138.7
5	130.0	129.8	155.9	156.2	155.8	155.8	155.6	155.8	155.8
6	107.9	107.9	90.4	90.3	90.4	90.2	90.5	90.3	90.1
7	160.9	160.9	161.5	161.2	161.3	161.6 ^{a)}	161.4	161.4 ^{a)}	161.5
8	112.3	112.8	106.4	104.2	107.6	106.4	108.2	107.1	106.2
9	153.6	153.6	154.2	154.0	154.2	154.1	154.2	154.3	154.3
10	113.1	113.1	103.8	103.8	104.0	103.4	103.9	103.9	103.5
1'	69.3	68.6	22.0	34.3	25.2	22.6	24.6	29.0	26.4
2'	208.1	209.1	63.3	211.2	78.5	78.5	76.6	75.4	76.0
3'	36.3	36.2	59.3	40.7	73.0	72.2	77.3	147.3	143.6
4'	18.1 ^{a)}	18.2 ^{a)}	19.1 ^{a)}	18.5	23.9 ^{a)}	22.1	20.3 ^{a)}	110.4	112.2
5'	19.0 ^{a)}	18.9 ^{a)}	24.8 ^{a)}	18.5	26.2 ^{a)}	22.1	21.0 ^{a)}	18.1	18.3
1''	171.7	165.0	—	—	—	172.6	—	—	172.3
2''	43.2	115.4	—	—	—	43.2	—	—	43.6
3''	25.7	158.4	—	—	—	26.2	—	—	25.5
4''	22.4	27.5	—	—	—	25.2 ^{b)}	—	—	22.2
5''	22.4	20.4	—	—	—	25.5 ^{b)}	—	—	22.2
5-OMe	—	—	56.0 ^{b)}	56.0	56.0 ^{b)}	55.9 ^{c)}	55.9 ^{b)}	55.9 ^{b)}	55.8 ^{a)}
7-OMe	56.4	56.4	56.1 ^{b)}	56.0	56.2 ^{b)}	56.1 ^{c)}	56.2 ^{b)}	56.1 ^{b)}	56.0 ^{a)}
OMe	—	—	—	—	—	—	49.4	—	—

Spectra were measured at 100 MHz in CDCl_3 and the values are given as δ ppm with TMS as internal standard. ^a–^c) Assignments in the same column may be interchangeable. The numbering of carbons is shown in the structures (for that of an isovaleryl unit of **5b** and **6b**, see 1).

of prenylcoumarins, in particular, those of rutaceous origin. In this report, the carbon signals of coumarins isolated from *M. paniculata* var. *omphalocarpa* leaves were assigned by the use of ^{13}C - ^1H correlation spectroscopy (COSY) and long range ^{13}C - ^1H COSY, and the results are shown in Table I.

In the previous paper, the first author pointed out the possible occurrence of several chemical races in *M. paniculata*, and specified Formosan and Indonesian races.⁸⁾ The Formosan race can be clearly distinguished from the Indonesian race by the absence of 5,7-dimethoxy-8-prenylcoumarins that are principal constituents of the latter.⁹⁾ The present chemical study revealed that coumarin constituents of var. *omphalocarpa* are mainly composed of 5,7-dimethoxy-8-prenylcoumarins. Therefore, with regard to the chemosystematic relation of var. *omphalocarpa* with the mother species (var. *paniculata*), it is presumed that this variety has a closer chemical relationship to the Indonesian race rather than to the Formosan race, which occurs geographically in proximity. Perhaps var. *omphalocarpa* is derived not from the Formosan race but from the one related to the Indonesian race from the chemosystematic point of view. *M. paniculata* is very widely distributed extending in the west to India, in the north to southern China and the Okinawa Islands, and in the south and east to New Guinea, New Caledonia and northern Australia.¹⁾ Thus, there may be other chemical types different from those referred to so far. The chemical investigation of *M. paniculata* of other localities is currently under way in order to clarify the chemical evolution of the genus *Murraya*.

Experimental

All melting points were measured on a Yanagimoto melting point apparatus and are uncorrected. Spectral data were obtained using the following apparatus: proton and carbon-13 nuclear magnetic resonance (^1H - and ^{13}C -NMR) spectra with a JEOL JNM GSX-400 (^1H , 400 MHz; ^{13}C , 100 MHz) spectrometer with tetramethylsilane (TMS) as internal standard; mass spectra (MS) with a JEOL SX-102A mass spectrometer; IR spectra with a JASCO FT/IR-8000 infrared spectrometer; UV spectra with a Shimadzu UV-240 spectrometer; optical rotations with a JASCO DIP-370 polarimeter. Column chromatography was carried out with the following materials: Wakogel C-200 or Merck Kieselgel 60 (eluted with benzene-acetone or hexane-ethyl acetate), Sephadex LH-20 (Pharmacia, eluted with $\text{MeOH}-\text{CHCl}_3$) and RP-8 reversed-phase silica gel (Merck, eluted with $\text{MeOH}-\text{H}_2\text{O}$). Thin-layer chromatography (TLC) was conducted on a 0.25 mm pre-coated silica gel plate (60GF₂₅₄, Merck), and spots were detected by inspection under short (254 nm) or long (360 nm) wavelength UV lights, or by the colors developed with 10% H_2SO_4 spraying followed by heating on a hot plate.

Plant Material The leaves of *M. paniculata* var. *omphalocarpa* were collected in 1988 in Lan Yu, Taiwan, and identified by one of the authors (F.-C. H.). A voucher specimen is on deposit at the Herbarium of Taiwan Forestry Research Institute, Heng-Chun, Taiwan.

Extraction and Isolation The dried leaves (2 kg) of *M. paniculata* var. *omphalocarpa* were extracted two times with distilled acetone at room temperature, and the combined extract was evaporated to dryness under reduced pressure to yield a greenish viscous syrup (127.4 g). The whole extract was dissolved in acetone and adsorbed on silica gel (120 g). The adsorbed material was transferred to a silica gel column (1 kg) packed in hexane (column size: 10 cm $\times$ 28 cm). The column was eluted with a solvent system of hexane-ethyl acetate increasing the amount of ethyl acetate gradually. Fractions of 500 ml each were collected and combined into twenty-two fractions on the basis of their TLC patterns: Fr. I (fr. 1—5; 1.25 g); Fr. II (fr. 6—15; 0.84 g); Fr. III (fr. 16—37; 0.05 g); Fr.

IV (fr. 38—82; 0.08 g), Fr. V (fr. 83—86; 14.12 g); Fr. VI (fr. 87—90; 11.4 g); Fr. VII (fr. 91—92; 4.09 g); Fr. VIII (fr. 93—103; 10.78 g); Fr. IX (fr. 104—107; 6.12 g); Fr. X (fr. 108—115; 5.97 g); Fr. XI (fr. 116—119; 3.76 g); Fr. XII (fr. 120—126; 4.53 g); Fr. XIII (fr. 127—135; 18.53 g); Fr. XIV (fr. 136—143; 4.17 g); Fr. XV (fr. 144—155; 4.22 g); Fr. XVI (fr. 156—163; 1.84 g); Fr. XVII (fr. 164—172; 2.55 g); Fr. XVIII (fr. 173—189; 12.39 g); Fr. XIX (fr. 190—203; 5.21 g); Fr. XX (fr. 204—220; 3.25 g); Fr. XXI (fr. 221—249; 5.30 g); Fr. XXII (fr. 250—270; 10.0 g). Fraction X was separated by silica gel column chromatography (3.6 cm $\times$ 12 cm) on elution with benzene-acetone (B-A), increasing the amount of acetone stepwise. Fractions of 200 ml each were collected. Fractions 3—5, eluted with 3%, 4% and 6% B-A, were combined and purified by repeated column chromatography over silica gel, Sephadex LH-20 and reversed-phase silica gel (RP-8) to give omphamurin isovalerate (**6b**) (28 mg). Fraction XIII was partitioned between MeOH (200 ml) and hexane (400 ml), and the MeOH layer was evaporated to dryness. The residue was subjected to Sephadex LH-20 column chromatography on elution with $\text{MeOH}-\text{CHCl}_3$ (2:1) in order to remove chlorophylls. The coumarin-rich fractions were collected and chromatographed over silica gel (150 g) on elution with the stepwise-gradient solvent system of B-A. Fractions eluted with 2% B-A were combined and further separated by RP-8 column chromatography to give 3.6 g of paniculatin (**1**) [mp 95—96°C; $[\alpha]_D^{25} + 94.3^\circ$]. Fractions eluted with 4% B-A afforded 3.0 g of 5,7-dimethoxy-8-(3'-methyl-2'-oxobutyl)-coumarin (**4**) [mp 131—132°C]. Fractions eluted with 6—8% B-A were rechromatographed over silica gel to give 1.29 g of (–)-sibiricin (**3**) [mp 150—152°C; $[\alpha]_D^{25} - 57.6^\circ$] and 0.41 g of omphalocarpin (**5c**) [mp 157—159°C; $[\alpha]_D^{25} - 48.9^\circ$]. Fraction XIV was subjected to Sephadex LH-20 column chromatography ($\text{MeOH}-\text{CHCl}_3$ 1:2 as eluant) followed by silica gel column chromatography on elution with the gradient solvent system of B-A to give 0.59 g of murpaniculol senecioate (**2**) and 109 mg of omphamurin (**6a**) [mp 125—126°C; $[\alpha]_D^{25} - 6.0^\circ$]. Fraction XVI was separated by silica gel column chromatography on elution with B-A followed by RP-8 column chromatography to give 5-methoxymurrayatin (**5b**) (118 mg). Fraction XXI was subjected successively to Sephadex LH-20 ($\text{MeOH}-\text{CHCl}_3$, 2:1) and silica gel (B-A) column chromatography to afford 0.58 g of mexotocin (**5a**) [mp 191—193°C; $[\alpha]_D^{25} - 36.9^\circ$].

Murpaniculol Senecioate (2) Colorless oil. $[\alpha]_D^{25} + 123.3^\circ$ (CHCl_3 , $c = 1.46$). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3027, 2977, 2940, 1734, 1613, 1267, 1252, 1142, 1119, 835. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 255 (3.73), 300 sh (4.06), 318 (4.19). ^1H -NMR (CDCl_3) δ : 1.04 (3H, d, $J = 6.7$ Hz, 4'- CH_3 or 5'- CH_3), 1.20 (3H, d, $J = 6.7$ Hz, 5'- CH_3 or 4'- CH_3), 1.89 (3H, d, $J = 1.4$ Hz, 4''- CH_3), 2.19 (3H, d, $J = 1.2$ Hz, 5''- CH_3), 2.97 (1H, hept, $J = 6.7$ Hz, 3'-H), 3.91 (3H, s, 7-O CH_3), 5.79 (1H, m, 2''-H), 6.26 (1H, d, $J = 9.5$ Hz, 3-H), 6.88 (1H, d, $J = 8.7$ Hz, 6-H), 7.03 (1H, s, 1'-H), 7.47 (1H, d, $J = 8.7$ Hz, 5-H), 7.62 (1H, d, $J = 9.5$ Hz, 4-H). ^{13}C -NMR (CDCl_3) δ : see Table I. EI-MS m/z (%): 358 (M^+ , 4), 287 (63), 205 (56), 83 (100). HR-MS: Calcd for $\text{C}_{20}\text{H}_{22}\text{O}_6$: 358.1416. Found: 358.1418.

5-Methoxymurrayatin (5b) Colorless oil. $[\alpha]_D^{25} + 55.9^\circ$ (CHCl_3 , $c = 2.400$). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm^{-1} : 3021, 2965, 1723, 1605, 1470, 1335, 1121. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 254 sh (3.98), 259 (4.02), 325 (4.16). ^1H -NMR (CDCl_3) δ : 0.67 (3H, d, $J = 6.5$ Hz, 4'- CH_3 or 5''- CH_3), 0.72 (3H, d, $J = 6.5$ Hz, 5''- CH_3 or 4''- CH_3), 1.30, 1.33 (3H each, s, 4'- CH_3 , 5''- CH_3), 1.82 (1H, hept, $J = 6.5$ Hz, 3''-H), 1.89 (1H, dd, $J = 7.2$, 14.6 Hz, 2''-H), 2.00 (1H, dd, $J = 7.0$, 14.6 Hz, 2''-H), 2.93 (1H, dd, $J = 2.3$, 13.9 Hz, 1'-H), 3.17 (1H, dd, $J = 10.7$, 13.9 Hz, 1'-H), 3.91, 3.94 (3H each, s, 5-, 7-O CH_3), 5.12 (1H, dd, $J = 2.3$, 10.7 Hz, 2'-H), 6.08 (1H, d, $J = 9.6$ Hz, 3-H), 6.29 (1H, s, 6-H), 7.94 (1H, d, $J = 9.6$ Hz, 4-H). ^{13}C -NMR (CDCl_3) δ : see Table I. EI-MS m/z (%): 392 (M^+ , 3), 290 (60), 275 (85), 249 (100), 219 (94), 161 (32). HR-MS: Calcd for $\text{C}_{21}\text{H}_{28}\text{O}_7$: 392.1835. Found: 392.1837. A pyridine solution (1 ml) of (–)-mexotocin (**5a**) (25 mg) and isovaleryl chloride (25 mg) was left overnight at room temperature, and then evaporated to dryness. The residue was purified by silica gel column chromatography on elution with B-A (19:1) to give 5-methoxymurrayatin (**5b**) as a colorless oil (23 mg). The semi-synthetic compound was identical with the natural compound in an optical rotation, IR and ^1H -NMR spectra.

Omphamurin Isovalerate (6b) Colorless needles from $\text{MeOH}-\text{H}_2\text{O}$, mp 112—120°C (dec.). $[\alpha]_D^{25} - 14.9^\circ$ (CHCl_3 , $c = 1.561$). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3021, 2965, 1723, 1605, 1470, 1333, 1252, 1138, 1123. UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (log ϵ): 253 sh (3.95), 259 (3.98), 323 (4.16). ^1H -NMR (CDCl_3) δ : 0.79 (6H, d, $J = 6.4$ Hz, 4'- CH_3 , 5''- CH_3), 1.85 (3H, s, 5'- CH_3), 1.95 (1H, hept, $J = 6.4$ Hz, 3''-H), 2.05—2.07 (2H, m, 2''- H_2), 3.04 (1H, dd, $J = 5.2$, 13.7 Hz, 1'-H), 3.19 (1H, dd, $J = 8.6$, 13.7 Hz, 1'-H), 3.92,

3.94 (3H each, s, 5- and 7-OCH₃), 4.82, 4.87 (1H each, m, 4'-H₂), 5.45 (1H, dd, $J=5.2, 8.6$ Hz, 2'-H), 6.13 (1H, d, $J=9.8$ Hz, 3-H), 6.30 (1H, s, 6-H), 7.97 (1H, d, $J=9.8$ Hz, 4-H). ¹³C-NMR (CDCl₃) δ : see Table I. EI-MS m/z (%): 374 (M⁺, 2), 272 (31), 242 (13), 219 (100), 161 (15). HR-MS: Calcd for C₂₁H₂₆O₆: 374.1730. Found: 374.1738. *Anal.* Calcd for C₂₁H₂₆O₆: C, 69.75; H, 7.02. Found: C, 69.86; H, 7.07. A pyridine solution (1 ml) of omphamurin (**6a**) (10 mg) and isovaleryl chloride (10 mg) was left overnight at room temperature, and then evaporated to dryness. The residue was purified by silica gel column chromatography on elution with B-A (19:1) to give omphamurin isovalerate (**6b**) as colorless needles (12 mg). The semi-synthetic compound was identical with natural omphamurin isovalerate in an optical rotation, IR and ¹H-NMR spectra.

Chemical Conversion of (–)-Sibiricin (3) into Omphamurin (6a)
Boron trifluoride etherate (0.2 ml) was added to a mixture of (–)-sibiricin (**3**) (50 mg) and anhydrous dimethylsulfoxide (5 ml), and the mixture was left for 2 h. The mixture was poured into ice-cold water and extracted with benzene. The benzene layer was washed successively with 5% potassium carbonate and water, dried over anhydrous sodium sulfate, and then evaporated. The residue was separated by a silica gel column chromatography to give 5 mg of omphamurin (**6a**), $[\alpha]_D^{25} -15.4^\circ$ (CHCl₃, $c=0.233$), and 5,7-dimethoxy-8-(3'-methyl-2'-oxobutyl)-coumarin (**4**) (18 mg).

Determination of the Absolute Stereochemistry of Omphamurin (6a) by Horeau's Method
Racemic α -phenylbutyric anhydride (400 mg) and omphamurin (**6a**) (50 mg) were dissolved in anhydrous pyridine (2 ml). The reaction mixture was left overnight. The excess anhydride was decomposed by adding ice-cold water (25 ml), and the aqueous solution was extracted with ethyl acetate (3 $\times$ 25 ml). The ethyl acetate extract was extracted with 5% sodium bicarbonate (3 $\times$ 20 ml). The alkaline extract was washed with chloroform and subsequently acidified with 10% hydrochloric acid. The free acid liberated was extracted with chloroform and worked-up in the usual manner. The free α -phenylbutyric acid was obtained from the chloroform solution on evaporation. Yield: 330 mg. $[\alpha]_D^{25} -0.43^\circ$ (MeOH, $c=22$).

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