The Chemical Composition of *Murraya paniculata*. The Structure of Five New Coumarins and One New Alkaloid and the Stereochemistry of Murrangatin and Related Coumarins†

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The structural determination of five new coumarins: murralonginol isovalerate (**1b**), isomurralonginol isovalerate (**2b**), murrangatin isovalerate (**6b**), minumicrolin isovalerate (**7b**), chloculol (**4a**), and a new indole alkaloid, paniculol (**18**), is described.

The relative configurations hitherto reported for the α-glycol moieties in murrangatin (*erythro*) and minumicrolin (*threo*) have been revised to *threo* for compound (**6a**) and *erythro* for compound (**7a**), respectively on the basis of NOE experiments performed on the acetonides (**6e**) and (**7e**). Furthermore, the absolute configuration of (—)-murrangatin (**6a**) has been shown to be [*R*, *R*] by analysis of the CD spectrum of tetrahydromurrangatin dibenzoate (**16b**). The reaction of phebalosin (**8**) with hydrochloric acid has also been re-examined.

We have systematically studied the chemical constituents of Rutaceous plants.[1] Furukawa has reported on the chemical composition of the leaves of *Murraya paniculata* (L.) Jack,[1b] collected in the Iriomote Islands, Okinawa, Japan, and on leaves of *M. exotica* L.[1c,d] cultivated at Higashiyama Zoo and Botanical Garden, Nagoya, Japan.

M. paniculata (L.) Jack.[2] and *M. exotica* L.[2] grow in Southern Asia as shrubs. The *M. exotica* plant had hitherto been considered to be identical with *M. paniculata*.[2] However, recent investigations[3] have led to the proposal that this species be reinstated as a distinct taxon. Moreover, both plants have been used as indigenous drugs[4] in India. In these circumstances, the study of the chemical composition of *M. paniculata* is of some interest.

Many research groups[3,5–7] have found that *M. paniculata* contains several kinds of coumarins and indole alkaloids. In this report, we describe the structural elucidation of five new coumarins: murralonginol isovalerate (**1b**), isomurralonginol isovalerate (**2b**), chloculol (**4a**), murrangatin isovalerate (**6b**), minumicrolin isovalerate (**7b**), and a new indole alkaloid, paniculol (**18**), derived from the root bark of *M. paniculata* collected at Ishigaki Island, Okinawa, in May.

Furthermore, we report on a revision of the reported relative configurations[7] of the α-glycol systems from (−)-murrangatin (*erythro*) and (+)-minumicrolin (*threo*) to *threo* for compound (**6a**) and *erythro* for compound (**7a**) basis of NOE experiments performed on their acetonides [compounds (**6e**) and (**7e**)]. That the absolute configuration of (−)-murrangatin (**6a**) is [*R*, *R*] was confirmed by analysis of the CD spectrum of tetrahydromurrangatin dibenzoate (**16b**), and a re-examination of the behaviour of phebalosin (**8**) on treatment with hydrochloric acid is described.

Results and Discussions

The five new coumarins (**1b**), (**2b**), (**4a**), (**6b**), and (**7b**) contain common features in their ^{1}H NMR spectra (Table). In particular, signals are evident in the ranges: δ 3.87–4.00 (3 H, s, OMe), 6.24–6.28 and 7.61–7.64 (1 H, d, *J* 9.4 Hz, 3- and 4-H of coumarin skeleton, respectively), and 6.84–6.91 and 7.35–7.43 (1 H, d, *J* 8.7 Hz, 6- and 5-H, *ortho*-coupled aromatics, respectively). Since all of the naturally occurring coumarins[8] isolated from Rutaceous plants have an oxygen function at C-7, we propose that these five new coumarins are the 8-substituted 7-methoxycoumarin derivatives, structure (**A**). In other words, structural elucidations performed on these five new coumarins can then be applied to determinations of their C-8-substituted groups.

Structure of Murralonginol Isovalerate (**1b**).—Murralonginol isovalerate (**1b**) was isolated as a pale yellow syrup. The molecular formula was established as $C_{20}H_{24}O_5$ by high resolution mass spectrometry. In the electron impact (EI) mass spectrum, two characteristic ions are evident at *m/z* 259 [$M - {}^{\cdot}COCH_2CHMe_2]^+$ and *m/z* 243 [$M - {}^{\cdot}OCOCH_2CHMe_2]^+$, suggesting that this new coumarin (**1b**) contains an isovaleryl group. This assumption is supported by the fact that, in the ^{1}H NMR spectrum (Table), there are signals at δ 0.79 (6 H, d) and in the range 1.87–2.05 (3 H, mult.). Further, two singlets at δ 2.01 and 1.52 (3 H) and two doublets at δ 4.93 and 4.88 (1 H, *J* 15.8 Hz) were observed, indicating the presence of a 2-substituted 3-methylbut-2-enyloxy group in the side chain. This deduction led us to conclude that this new coumarin should be depicted by the structure (**1b**).

In 1986, Kinoshita, Sankawa, and co-workers[6b] isolated murralongin (**3**) from the same plant collected in Taiwan and established its structure to be that given in formula (**3**). We attempted to convert murralongin (**3**) into murralonginol isovalerate (**1b**). Reduction of murralongin (**3**) with sodium borohydride followed by treatment with isovaleryl chloride in pyridine gave the desired product (**1b**), which was identical with a sample of naturally occurring murralonginol isovalerate. Since this coumarin belongs to a new type of coumarin, we wish to designate the mother alcoholic coumarin (**1a**) as murralonginol, although it has not been isolated from the natural source until now. This proposal allows us to name our coumarin (**1b**) as murralonginol isovalerate.

Structure of Isomurralonginol Isovalerate (**2b**).—Isomurralonginol isovalerate (**2b**) was obtained as a pale yellow syrup,

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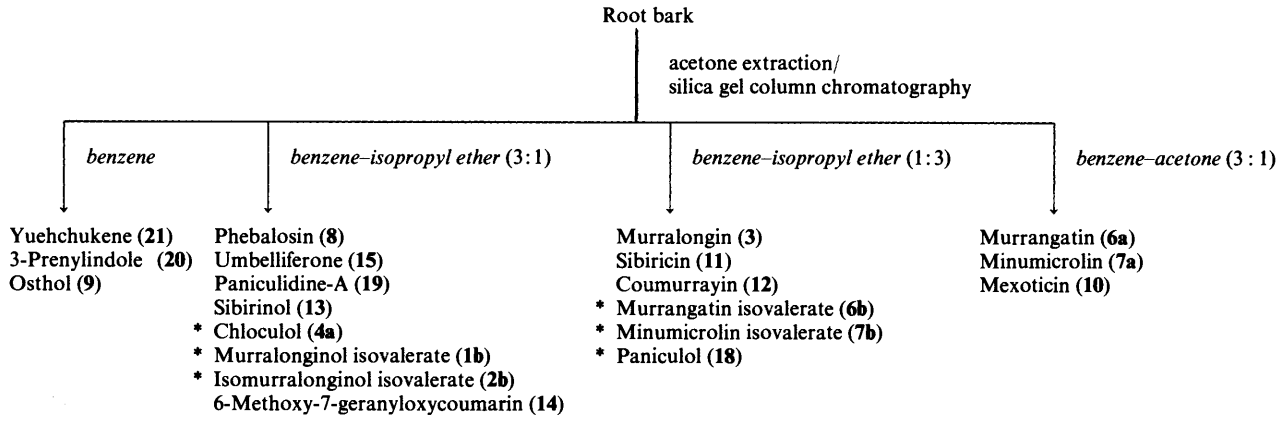


Scheme. Natural products isolated from *Murraya paniculata*. An asterisk * denotes new compounds.

Table. ^{1}H NMR (270 MHz) spectra of some new coumarins and analogues.[a]

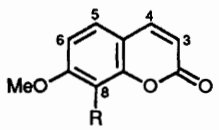
	3-H	4-H	5-H	6-H	O-CH_3	1′-H	2′-H	allyl $-CH_3$	*exo* $=CH_2$	OH	Others
(1a)	6.25 d (9.4)	7.65 d (9.4)	7.39 d (8.7)	6.90 d (8.7)	3.90 s			1.50 s 2.01 s		1.82	4.40 (d, 12.1), 4.31 (d, 12.1)
(1b)*	6.24 d (9.4)	7.63 d (9.4)	7.37 d (8.7)	6.86 d (8.7)	3.87 s			1.52 s 2.01 s			4.88 (d, 15.8), 4.93 (d, 15.8) 0.79 (6 H, d, 6.4), 1.87–2.05 (3 H, m)
(2b)*	6.24 d (9.4)	7.62 d (9.4)	7.35 d (8.7)	6.84 d (8.7)	3.88 s			1.70 s	4.88 s 4.91 s		4.50 (t, 7.4), 4.66 (dd, 10.8, 7.4), 4.80 (dd, 10.8, 7.4) 0.82 (6 H, d, 6.7), 1.93 m, 2.07 (2 H, m)
(4a)*	6.28 d (9.4)	7.64 d (9.4)	7.43 d (8.7)	6.91 d (8.7)	4.00 s	5.56 t (10.0)	4.95 d (10.0)	2.01 s	5.12 s 5.22 s	3.37 br d (10.0)	
(5a)	6.27 d (9.4)	7.61 d (9.4)	7.42 d (8.7)	6.86 d (8.7)	3.97 s	5.79 d (8.0)	5.21 s	1.64 s	4.66 s 4.83 s	2.76 br s	
(6a)	6.25 d (9.4)	7.62 d (9.4)	7.39 d (8.7)	6.87 d (8.7)	3.97 s	5.30 t (8.7)	4.51 d (8.7)	1.78 s	4.58 s 4.65 s	3.74 br 3.19 br	
(6b)*	6.26 d (9.4)	7.61 d (9.4)	7.39 d (8.7)	6.87 d (8.7)	4.00 s	5.53 dd (11.4, 7.7)	5.76 d (7.7)	1.75 s	4.73 s 4.77 s	3.55 br d (11.4)	2.27 (2 H, m), 2.15 (1 H, m), 0.96 (3 H, d, 6.7), 0.95 (3 H, d, 6.7)
(6c)	6.24 d (9.4)	7.59 d (9.4)	7.37 d (8.7)	6.84 d (8.7)	3.95 s	6.40 d (8.1)	4.93 d (8.1)	1.75 s	4.71 s 4.76 s	2.63 br s	2.25 (2 H, m), 2.17 (1 H, m), 0.87 (3 H, d, 6.7), 0.86 (3 H, d, 6.7)
(7a)	6.25 d (9.4)	7.63 d (9.4)	7.40 d (8.7)	6.89 d (8.7)	3.97 s	5.41 dd (7.0, 10.0)	4.51 d (7.0)	1.88 s	4.97 s 4.98 s	2.23 br 3.64 br d (10.0)	
(7b)*	6.27 d (9.4)	7.62 d (9.4)	7.38 d (8.7)	6.87 d (8.7)	4.00 s	5.51 dd (11.4, 8.7)	5.67 d (8.7)	1.93 s	5.09 s 5.14 s	3.53 br d (11.7)	1.90 (2 H, m), 1.75 (1 H, m) 0.64 (3 H, d, 6.4), 0.63 (3 H, d, 6.4)
(7c)	6.26 d (9.4)	7.60 d (9.4)	7.39 d (8.7)	6.87 d (8.7)	3.95 s	6.49 d (7.1)	4.83 d (7.1)	1.88 s	4.91 s 5.00 s	2.32 br s	2.20 (2 H, m), 2.08 (1 H, m), 0.87 (6 H, d, 6.4)

[a] Values (ppm) in $CDCl_3$. Figures in parentheses are coupling constants in Hz. An asterisk indicates new coumarins.

$[\alpha]_D$ +14.5° ($CHCl_3$). The molecular formula, $C_{20}H_{24}O_5$, was established by high resolution MS indicating that compound (**2b**) is a structural isomer of murralonginol isovalerate (**1b**). The existence of an isovaleryl group in the molecule was also confirmed by MS (EI) [*m/z* 259 (M − $^{\cdot}COCH_2CHMe_2$)$^+$ and 242 (M − $HOCOCH_2CHMe_2$)$^+$] and by ^{1}H NMR spectroscopy [δ_H 0.82 (6 H, d, *J* 6.7 Hz), 1.93 (1 H, m), and 2.07 (2 H, m)]. Further, in the ^{1}H NMR spectrum, the material (**2b**) shows a 3 H singlet at δ 1.70, a 1 H triplet (*J* 7.4 Hz) at δ 4.50, two 1 H double doublets (*J* 10.8 and 7.4 Hz) at δ 4.66 and 4.80, and two 1 H singlets at δ 4.88 and 4.91 (side chain signals). Since these six signals are attributable to a 2-substituted 3-methylbut-3-enyloxy group, the basic structure of isomurralonginol isovalerate could be depicted as given by formula (**2b**). The ^{13}C NMR spectral data of this coumarin supported our deduction (see Experimental section). However, the absolute configuration of this coumarin (**2b**) remained as a problem to be solved.

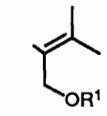
Since we (H. F.) have already established the structure of isomurralonginol acetate (**2c**) [1c] and its nicotinate (**2d**) [1b] having a 2-substituted 3-methylbut-3-enyloxy group we designated the mother alcoholic coumarin (**2a**) as isomurralonginol; our new coumarin (**2b**) can therefore be named as isomurralonginol isovalerate.

Structure of Chloculol (**4a**).—Chloculol (**4a**) was obtained as colourless prisms, m.p. 149–151 °C, $[\alpha]_D$ −23° ($CHCl_3$). The chemical ionization mass spectrum, MS (CI), using ammonia as a reactant gas showed a molecular ion peak at *m/z* 312 [M + NH_4]$^+$ and an isotope peak at *m/z* 314 in the ratio *ca.* 3:1, suggesting the presence of a chlorine atom in the molecule. Treatment of chloculol (**4a**) with acetic anhydride in pyridine gave the mono-acetate (**4b**) as a colourless oil. The molecular formula of the original coumarin (**4a**) was established as $C_{15}H_{15}ClO_4$ by high resolution MS on the mono-acetate (**4b**). In the ^{1}H NMR spectrum of chloculol (**4a**), the presence in the



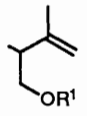
(A)

R =



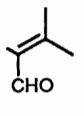
(1)

a R^1 = H
b R^1 = isovaleryl

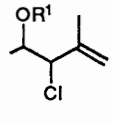


(2)

a R^1 = H
b R^1 = isovaleryl
c R^1 = Ac
d R^1 = py – CO

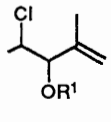


(3)



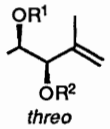
(4)

a R^1 = H
b R^1 = Ac



(5)

a R^1 = H
b R^1 = Ac

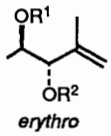


threo

(6)

a $R^1 = R^2$ = H
b R^1 = H, R^2 = isovaleryl
c R^1 = isovaleryl, R^2 = H
d $R^1 = R^2$ = isovaleryl
e $R^1 = R^2 = \rangle CMe_2$

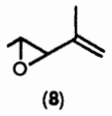
R =



erythro

(7)

a $R^1 = R^2$ = H
b R^1 = H, R^2 = isovaleryl
c R^1 = isovaleryl, R^2 = H
d $R^1 = R^2$ = isovaleryl
e $R^1 = R^2 = \rangle CMe_2$



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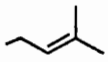

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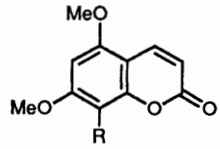

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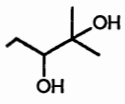

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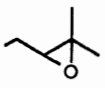

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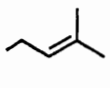

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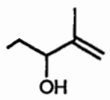

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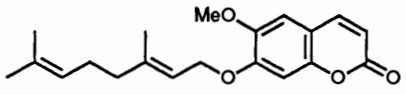

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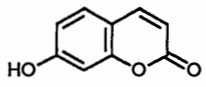

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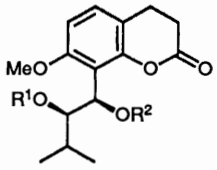
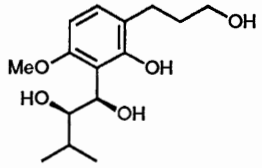


(16)

a $R^1 = R^2$ = H
b $R^1 = R^2$ = PhCO



(17)

molecule of an *exo*-methylene group, an allylic methyl group, and a hydroxy group could be shown by the appearance of two 1 H singlets at δ 5.12 and 5.22, a 3 H singlet at δ 2.01, and a 1 H doublet (*J* 10 Hz) at δ 3.37, along with a 1 H doublet (*J* 10 Hz) at δ 4.95 and a 1 H triplet at δ 5.56, which was shifted downfield to δ 6.71 (d, *J* 10 Hz) in the ^{1}H NMR spectrum of the acetate (**4b**), showing that the signal could be assigned to a proton adjacent to a hydroxy group. These assignments, together with the observation of a mass fragment peak at *m/z* 205 ascribed to ion $[M - {}^{\cdot}CHClCMe{=}CH_2]^+$, allowed us to deduce that the coumarin has a –CH(OH)–CHCl–CMe=CH_2 fragment in the molecule. These considerations led us to conclude that the structure of chloculol should be depicted by the formula (**4a**) neglecting stereochemical features.

At this stage, we wondered if chloculol (**4a**) might be formed during isolation from optically active phebalosin (**8**),[9] which contains an oxirane ring, and has only been isolated to date as a racemate from natural sources. We thus examined the ring cleavage of the oxirane ring of phebalosin (**8**) under acid conditions. Treatment of compound (**8**) with a catalytic amount of conc. hydrochloric acid in chloroform at room temperature for 30 min gave a chlorohydrin (**5a**), m.p. 131–133 °C, as sole product, in contrast to Talapatra's experiment (*vide infra*).[10] The ^{1}H NMR spectrum of this chlorohydrin (**5a**) showed a similar signal pattern to that of chloculol (**4a**) (see Table). However, in the MS (EI) spectrum, characteristic differences between chloculol (**4a**) and the chlorohydrin (**5a**) were observed. While a former shows a characteristic fragment peak at *m/z* 205, the formation of which could be explained by cleavage at the benzylic position of chloculol (**4a**) as described above, the latter (**5a**) exhibits corresponding fragment peaks at *m/z* 224 and 226 (3:1). This fact strongly indicates that the position of the chlorine atom is different between chloculol (**4a**) and the chlorohydrin (**5a**), *i.e.* compound (**5a**) has a chlorine atom at C-1′. The fact that chloculol (**4a**) is not an oxirane ring-opening product from optically active phebalosin means that chloculol (**4a**) is a true natural metabolite.

Stereochemistry of Murrangatin (**6a**) *and Minumicrolin* (**7a**).—In 1972, Khosa[7] isolated murrangatin from *M. paniculata* and proposed the basic structure 7-methoxy-8-(1,2-dihydroxy-3-methylbut-3-enyl)coumarin for the molecule. Later, Talapatra *et al.*[10] treated phebalosin (**8**),[9] m.p. 132 °C, with 1.5M hydrochloric acid in dioxane at room temperature and obtained an α-glycol product, m.p. 132 °C, instead of a chlorohydrin. This α-glycol was found to be identical with a sample of racemic murrangatin. Since, in the ^{1}H NMR spectrum, the value of the coupling constant of the signal due to vicinal protons in the original oxirane ring of phebalosin (**8**) was observed to be small (*J* 2.0 Hz), they claimed the relative stereochemistry of the α-glycol function in murrangatin to be the *erythro* configuration (**7a**).

On the other hand, in 1984, Herz and collaborators[11] isolated minumicrolin, m.p. 132–135 °C, from *Micromelum minutum* (Rutaceae). Since minumicrolin was a diastereoisomeric isomer of murrangatin, they allocated the *threo* configuration (**6a**) to minumicrolin.

Given these circumstances, we wonder why Talapatra *et al.*[10] obtained, on treatment of phebalosin (**8**) with 1.5M hydrochloric acid in dioxane an α-glycol which they found to be identical with natural murrangatin, whereas in our case described above, phebalosin (**8**) gave the chlorohydrin (**5a**) as sole product on treatment with hydrochloric acid in chloroform. In addition, the experimental results on the structural elucidation of chloculol (**4a**) cast doubt upon the *erythro* configuration (**7a**)[10] reported for murrangatin itself. We therefore attempted to obtain confirmatory evidence on the relative configurations of the α-glycol.

Treatment of murrangatin and minumicrolin isolated in this work with acetone in the presence of a catalytic amount of toluene-*p*-sulphonic acid gave the corresponding acetonides (**6e**) and (**7e**), respectively. Differential NOE experiments on these acetonides revealed the following facts. In the case of minumicrolin acetonide, irradiation of 1′-H at δ 6.11 causes a 15.7% enhancement of the signal attributable to 2′-H at δ 4.97; by contrast, irradiation of 2′-H causes a 20% enhancement of the 1′-H signal. On the other hand, in the case of murrangatin acetonide, the NOE enhancement could not be observed, neither by irradiation of 1′-H at δ 5.57 or of 2′-H at δ 5.01. Since this spectral evidence demonstrates precisely that vicinal protons adjacent to the oxygen atoms of the acetonide ring in the minumicrolin acetonide molecule should be *cis* disposed, the structure of minumicrolin must be represented by the *erythro* formula (**7a**), not by the *threo* formula (**6a**) as previously reported.[11] Thus, in the case of murrangatin, the *erythro* formula (**7a**) proposed by Talapatra[10] should be revised to the *threo* formula (**6a**).

In the formation of the α-glycol from the oxirane ring in phebalosin (**8**), following Talapatra's experiment,[10] the possibility of double inversions owing to formation of the chlorohydrin (**5a**) followed by replacement of a chloride anion with a hydroxide anion and/or a water molecule could not be excluded because the reaction site was benzylic. We therefore attempted to provide a definitive solution to this problem.

We first re-examined Talapatra's experiment.[10] Treatment of phebalosin (**8**) under the reported conditions[10] gave *threo*-murrangatin (**6a**) as the major product in 50% yield, along with the chlorohydrin (**5a**), murralongin[6b] (**3**), and *erythro*-minumicrolin (**7a**) in 25, 17, and 8% yields, respectively. Moreover, further treatment of the chlorohydrin (**5a**) under the same conditions yielded *threo*-murrangatin (**6a**) and murralongin (**3**) in 43 and 29% yields, respectively. These experimental facts clearly indicate that the formation of murrangatin (**6a**) following reaction of phebalosin (**8**) under Talapatra's conditions[10] should include a double inversion process.

The absolute stereochemistry of the α-glycol part of murrangatin (**6a**) and minumicrolin (**7a**) has remained an outstanding problem until now; we therefore tried to establish the stereochemistry of murrangatin (**6a**) at this stage. Prior to establishment of the absolute configuration, the optical purity of murrangatin (**6a**), m.p. 116 °C, $[\alpha]_D$ −10° ($CHCl_3$), isolated in this work, was examined by means of its ^{1}H NMR spectrum recorded in deuteriochloroform containing a chiral shift reagent, tris-[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato] europium(III), Eu(hfc)$_3$. We have to date gained sufficient experience in order to obtain a mixture of enantiomers as the chemical constituents from several Rutaceous plants. Such a spectral examination disclosed that the optical purity of murrangatin (**6a**), $[\alpha]_D$ −10°, isolated from this plant consisted of a mixture of each enantiomeric component in the ratio 3:1.

In the case of the coumarins, the confirmation of the absolute configuration in the side chain from the results of CD experiments is difficult in itself, because the direction of a given axis of the coumarin skeleton could not be easily decided upon. In other words, the sign of the Cotton effect in the CD spectrum of a coumarin derivative does not reflect the absolute configuration of the chiral centre in its side chain. We therefore applied the dibenzoate rule[12] to 3,4,3′,4′-tetrahydromurrangatin dibenzoate (**16b**).

Catalytic hydrogenation of an ethanolic solution of (−)-murrangatin (**6a**) on platinum oxide gave 3,4,3′,4′-tetrahydromurrangatin (**16a**) along with a small amount of the tetraol (**17**). Treatment of the tetrahydromurrangatin (**16a**) with benzoyl chloride in pyridine gave the dibenzoate (**16b**). In the CD spectrum,[12] this dibenzoate (**16b**) exhibited negative

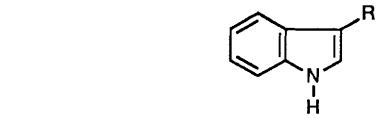
chirality (see Experimental section). Consequently, the absolute configuration of the two chiral centres in the (−)-murrangatin molecule was found to be [*R*, *R*], as shown in the formula (**6a**). Studies on the absolute stereochemistry of minumicrolin (**7a**) (*erythro* isomer) are now in progress.

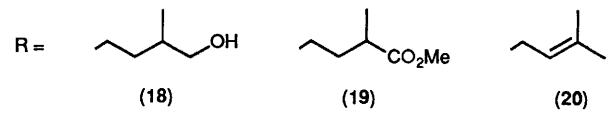
Structures of Murrangatin Isovalerate (**6b**) *and Minumicrolin Isovalerate* (**7b**).—Two new coumarins were isolated as colourless prisms, m.p. 100–103 °C, $[\alpha]_D$ −2.97° ($CHCl_3$) and a colourless oil, $[\alpha]_D$ +40.9° ($CHCl_3$), respectively. The MS (CI) spectra of both coumarins, using isobutane or ammonia as a reagent gas, suggested that both have the same molecular weight 360. The UV and IR spectra of these compounds closely resemble each other. The ^1H NMR spectra of these coumarins also exhibit signals attributable to an isovaleryloxy group (see Table). Moreover, each coumarin also shows an allylic methyl group, a hydroxy group, a vinylidene group, a proton adjacent to a hydroxy group, and a proton adjacent to an ester group. These spectral data clearly exhibit that both coumarins have a 1-substituted 3-methylbut-3-enyl group, the C-1 or C-2 of which were occupied by a hydroxy or an isovaleryl ester group. These spectral data suggest that these coumarins are diastereoisomeric isomers about their two oxygen functions in relation to each other. In other words, the structures of these coumarins should be depicted either by a pair of formulae (**6b**) and (**7b**) or by another pair of formulae (**6c**) and (**7c**).

These descriptions led us to suppose that two of our coumarins could be monovaleryl esters of murrangatin (**6a**) and minumicrolin (**7a**). In order to establish the location of the ester residue in our crystalline coumarin, differential NOE experiments (400 MHz) were carried out. Irradiation of the signal corresponding to one of the vinylidene protons at δ 4.73 gave a 10% enhancement of the signal at δ 5.76, illustrating that the isovaleryloxy group is located at the C-2′ position in the 3-methylbut-3-enyl side chain. There remained only the decision as to whether the structure of the crystalline coumarin should be represented by structure (**6b**) or (**7b**).

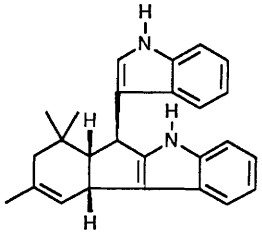
In order to yield confirmatory evidence for the structure of the crystalline coumarin, we treated murrangatin (**6a**) with isovaleryl chloride in pyridine to give the two mono-isovalerates (**6b**) and (**6c**). One of these mono-esters, (**6b**), was found to be identical with the naturally occurring crystalline coumarin; we assign it the name murrangatin isovalerate. The other mono-isovalerate should therefore be assigned the structure of 1′-isovaleryl murrangatin, compound (**6c**). It should be noted here that in the ^1H NMR spectra of these mono-esters (**6b**) and (**6c**), the signals due to the proton adjacent to an ester group have characteristically different chemical shifts, *i.e.* δ 5.76 (d, *J* 7.7 Hz) on murrangatin isovalerate (**6b**) and δ 6.40 (d, *J* 8.1 Hz) on 1′-isovaleryl murrangatin (**6c**). Subsequently, in order to establish the structure of another natural oily coumarin, minumicrolin (**7a**) was treated with isovaleryl chloride in pyridine to give two mono-isovalerates (**7b**) and (**7c**) along with a diester (**7d**). One of these two mono-esters, (**7b**), was found to be identical with the natural oily coumarin, and to it we assign the name minumicrolin isovalerate. The evidence for the position of the ester function in (**7b**) comes from a comparative observation of the ^1H NMR spectra of these two mono-isovaleryl coumarins (**7b**) and (**7c**). In the ^1H NMR spectrum, coumarin (**7b**) shows a signal due to a proton adjacent to an ester group at δ 5.67 (d, *J* 8.7 Hz) but that of the other mono-isovalerate (**7c**) is observed at δ 6.49 (d, *J* 7.1 Hz). Taking into account the difference between the chemical shift due to the corresponding signal of murrangatin isovalerate (**6b**) and that of murrangatin 1′-isovalerate (**6c**), these spectral data allow us to conclude that the ester group of (**7b**) is situated at the C-2′ position of minumicrolin (**7a**). Thus, the structure of minumicrolin isovalerate should be depicted by the formula (**7b**)

Structure of Paniculol (**18**).—Paniculol (**18**) was isolated as a colourless oil, $[\alpha]_D$ +11° ($CHCl_3$). The molecular formula was established as $C_{13}H_{17}NO$ by high resolution mass spectrometry.





(18) (19) (20)



(21)

The UV spectrum (λ_{max} 223, 274, 282, and 291 nm) showed a close resemblance to that of paniculidine-A (**19**),[6a] previously isolated from the same plant by Sankawa *et al.*, thus suggesting an indole skeleton for the compound. The ^1H NMR signals due to ABCD-type protons at δ 7.34 (1 H, d, *J* 8 Hz), 7.60 (1 H, d, *J* 8 Hz), 7.11 (1 H, dt, *J* 8 and 1.5 Hz), and 7.18 (1 H, dt, *J* 8 and 1.5 Hz) and the signal at δ 6.97 (1 H, d) coupled with an NH proton at δ 7.93 indicate the presence of a 3-substituted indole nucleus in this alkaloid. Analysis of the remaining ^1H NMR signals (see Experimental section) together with the observation of mass fragment ions at *m/z* 130 $[M - C_4H_9O]^+$ as a base peak and an IR band at ν_{max} 3 480 cm^{-1} (OH) led us to assign the structure (**18**) to paniculol. In agreement with this proposition, treatment of paniculidine-A (**19**) with lithium aluminium hydride in ether gave compound (**18**), which was found to be identical with paniculol by ^1H NMR, UV, and IR spectral comparisons. These data indicated the structure of paniculol to be formula (**18**), except for the stereochemistry. A synthesis of this compound has been reported by Sankawa and Kinoshita.[6a] However, this is the first reported occurrence from natural sources.

Other compounds isolated from the same plant material were characterized as murralongin (**3**),[6b] murrangatin (**6a**),[7] minumicrolin (**7a**),[11] phebalosin (**8**),[9] osthol (**9**),[13] umbelliferone (**15**),[14] paniculidine-A (**19**),[6a] and yuehchukene (**21**)[5b] by comparison of their ^1H NMR, IR, UV, and /or mass spectra with those of authentic samples. The physical constants and spectroscopic data (UV, IR, and/or ^1H NMR spectra) of compounds (**10**)–(**14**), and (**20**) were in agreement with those described in the literature for mexoticin,[15] sibiricin,[16] coumurrayin,[17] sibirinol,[18] 6-methoxy-7-geranyloxycoumarin,[19] and 3-prenylindole,[20] respectively.

Experimental

M.p.s were measured on a micromelting point hot-stage apparatus (Yanagimoto). ^1H and ^{13}C NMR spectra were recorded on GX-270 and GX-400 (JEOL) spectrometers, respectively, in $CDCl_3$ unless otherwise stated. Chemical shifts are shown in δ-values (ppm) with tetramethylsilane (TMS) as

an internal reference. MS (EI) were recorded on an Hitachi M-52 spectrometer with direct inlet system, and MS (CI) and high resolution mass spectra with an Hitachi M-80 spectrometer. UV spectra were determined in methanol and IR spectra were recorded in $CHCl_3$. Ether refers to diethyl ether throughout.

Extraction and Separation.—The dried root bark (250 g) of *Murraya paniculata* (L.) Jack, collected at Ishigaki Island, Okinawa, in May 1978 was extracted with acetone at room temperature (× 3), and the combined extracts were evaporated under reduced pressure. The residue (2.8 g) was subjected to silica gel column chromatography with successive elution with benzene, benzene–isopropyl ether (3:1–1:3), and benzene–acetone (3:1) to yield four fractions. Each fraction was further subjected to silica gel preparative TLC developed with appropriate combinations of acetone, benzene, hexane, isopropyl ether, and chloroform to yield the following components (see the Scheme).

First fraction: yuehchukene (**21**), 4 mg; 3-prenylindole (**20**), 5 mg; and osthol (**9**), 19 mg.

Second fraction: phebalosin (**8**), 287 mg; umbelliferone (**15**), 2 mg; paniculidine-A (**19**), 34 mg; sibirinol (**13**), 8 mg; 6-methoxy-7-geranyloxycoumarin (**14**), 3 mg; chloculol (**4a**), 5 mg; murralonginol isovalerate (**1b**), 2 mg; and isomurralonginol isovalerate (**2b**), 18 mg.

Third fraction: murralongin (**3**), 23 mg; sibiricin (**11**), 10 mg; coumurrayin (**12**), 2 mg; murrangatin isovalerate (**6b**), 8 mg; minumicrolin isovalerate (**7b**), 2 mg; and paniculol (**18**), 7 mg.

Fourth fraction: murrangatin (**6a**), 38 mg; minumicrolin (**7a**), 55 mg; and mexoticin (**10**), 24 mg.

Murralonginol Isovalerate (**1b**).—This was isolated as a pale yellow syrup; λ_{max} 258 and 323 nm; ν_{max} 1 720 (CO) and 1 600 cm^{-1} (C=C); δ_H: see Table; *m/z* (EI) 344 (M^+, 8%) 260 (23), 259 (96), 243 (36), 242 (97), 231 (41), 227 (21), 199 (22), 189 (100), 149 (21), 131 (33), and 115 (21) (Found: M^+, 344.1650. Calc. for $C_{20}H_{24}O_5$: M^+, 344.1622).

Murralongin (**3**).—These were colourless prisms; m.p. 132–134 °C (ether); λ_{max} 235 and 322 nm; ν_{max} 1 720 (CO), 1 670 (C=C), and 1 600 cm^{-1} (C=C); δ_H 1.79 (3 H, s, 3′-Me), 2.43 (3 H, s, 3′-Me), 3.83 (3 H, s, OMe), 6.23 (1 H, d, *J* 9.4 Hz, 3-H), 6.90 (1 H, d, *J* 8.7 Hz, 6-H), 7.45 (1 H, d, *J* 8.7 Hz, 5-H), 7.65 (1 H, d, *J* 9.4 Hz, 4-H), and 10.22 (1 H, s, HC=O); *m/z* (EI) 258 (M^+, 100%), 215 (92), 201 (32), 199 (49), 187 (68), 171 (38), and 159 (26).

Reduction of Murralongin (**3**).—Sodium borohydride (30 mg) was added to a methanolic solution (3 ml) of compound (**3**) (9 mg) in an ice–bath and the mixture was stirred for 5 min at room temperature. The solvent was evaporated and the residue purified by preparative TLC (silica gel; acetone–hexane, 1:2) to yield murralonginol (**1a**) (9 mg); λ_{max} 258, 323, and 341sh nm; ν_{max} 1 720 (CO) and 1 600 cm^{-1} (C=C); δ_H: see Table; *m/z* (EI) 260 (M^+, 67%) 245 (58), 242 (25), 231 (49), 227 (22), 217 (59), 203 (40), 189 (100), 171 (26), 131 (39), and 115 (42) (Found: M^+, 260.1023. Calc. for $C_{15}H_{16}O_4$: M^+, 260.1047).

Reaction of Murralonginol (**1a**) *with Isovaleryl Chloride.*—A solution of compound (**1a**) and isovaleryl chloride (20 mg) in pyridine (1 ml) was allowed to stand overnight at room temperature. The mixture was concentrated and the residue subjected to silica gel column chromatography. Elution with acetone–hexane (1:2) yielded compound (**1b**) as a pale yellow oil (11 mg), which was shown to be identical with natural murralonginol isovalerate by IR, ^1H NMR and mass spectroscopic comparisons.

Isomurralonginol Isovalerate (**2b**).—This was isolated as a pale yellow syrup; $[\alpha]_D$ +14.5° (*c* 0.13 in $CHCl_3$); λ_{max} 218sh, 247, 257, and 322 nm; ν_{max} 1 730 (CO) and 1 600 cm^{-1} (C=C); δ_H: see Table; δ_C 22.17 (q), 22.26 (2q), 25.61 (d), 40.69 (d), 43.48 (t), 56.05 (q), 64.13 (t), 107.86 (d), 111.69 (t), 113.16 (d), 113.16 (s), 116.32 (s), 127.59 (d), 142.55 (s), 143.76 (d), 153.63 (s), 160.75 (s), 161.16 (s), and 172.98 (s); *m/z* (EI) 344 (M^+), 259, 242 (100%), 230 (34), 227 (34), 211 (36), 199 (41), 189 (34), 171, 151, and 131 (Found: M^+, 344.1644. Calc. for $C_{20}H_{24}O_5$: M^+, 344.1623).

Chloculol (**4a**).—This was isolated as colourless prisms; m.p. 149–151 °C (acetone); $[\alpha]_D$ −23° (*c* 0.14 in $CHCl_3$); λ_{max} 247, 258, and 322 nm; ν_{max} 1 730 (CO) and 1 610 cm^{-1} (C=C); δ_H: see Table; *m/z* (EI) 206 (13%), 205 (100), 203 (9), 175 (19), 162, 149 (11), and 147; *m/z* (CI) 312 $[M + NH_4]^+$.

Chloculol Acetate (**4b**).—A mixture of compound (**4a**) (1.2 mg), acetic anhydride (1 ml), and pyridine (1 drop) was allowed to stand overnight at room temperature, and was then poured into ice–water, stirred for 30 min, neutralized with $NaHCO_3$, and extracted with $CHCl_3$. The extract was dried with anhydrous $MgSO_4$, and concentrated to dryness. The residue was subjected to silica gel preparative TLC to give compound (**4b**) quantitatively as a colourless oil; λ_{max} 248, 257, and 321 nm; ν_{max} 1 735 (CO) and 1 610 cm^{-1} (C=C); δ_H 1.94 (3 H, s, 3′-Me), 1.99 (3 H, s, COMe), 3.99 (3 H, s, OMe), 5.05 (1 H, s, C=CH_2), 5.24 (1 H, s, C=CH_2), 5.34 (1 H, d, *J* 10 Hz, 2′-H), 6.27 (1 H, d, *J* 9.4 Hz, 3-H), 6.71 (1 H, d, *J* 10 Hz, 1′-H), 6.88 (1 H, d, *J* 8.7 Hz, 6-H), 7.43 (1 H, d, *J* 8.7 Hz, 5-H), and 7.62 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (EI) 338–336 (M^+, 1:3) 301, 259, 247, 206, 205 (100%), 175, 162, and 147 (Found: M^+, 336.0785. Calc. for $C_{17}H_{17}O_5Cl$: M^+, 336.0764).

Oxirane Ring Cleavage of Phebalosin (**8**) *with* HCl.—A solution of compound (**8**) (10 mg) in chloroform and (4 ml) and conc. HCl (2 drops) was stirred for 30 min, before being neutralized with $NaHCO_3$ then concentrated to dryness. The residue was subjected to silica gel preparative TLC developed with acetone–hexane (1:2) to yield a chlorohydrin (**5a**) (11 mg, 98%) as colourless prisms, m.p. 131–133 °C (acetone); λ_{max} 253, 261, and 321 nm; ν_{max} 1 735 (CO) and 1 610 cm^{-1} (C=C); δ_H: see Table; *m/z* (EI) 258, 224–226 (3:1), 209, 189, 160 (100), and 131.

Acetylation of Chlorohydrin (**5a**).—Compound (**5a**) (11 mg) was acetylated with acetic anhydride in pyridine under the same conditions to afford compound (**5b**) (11 mg, 94%) as colourless prisms, m.p. 141–144 °C (acetone); λ_{max} 254, 260, 298sh, 323, and 336sh nm; ν_{max} 1 735 (CO) and 1 610 cm^{-1} (C=C); δ_H 1.56 (3 H, s, 3′-Me), 2.16 (3 H, s, COMe), 4.01 (3 H, s, OMe), 4.72 (1 H, s, C=CH_2), 4.98 (1 H, s, C=CH_2), 5.92 (1 H, br s, 1′-H), 6.23 (1 H, br s, 2′-H), 6.26 (1 H, d, *J* 9.4 Hz, 3-H), 6.86 (1 H, d, *J* 8.7 Hz, 6-H), 7.43 (1 H, d, *J* 8.7 Hz, 5-H), and 7.62 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (EI) 336–338 (M^+, 3:1), 301, 268, 266, 226, 224 (100%), 189, 188, 160, and 131 (Found: M^+, 336.0770. Calc. for $C_{17}H_{17}O_5Cl$: M^+, 336.0763).

Treatment of Phebalosin (**8**) *under Talapatra's Conditions.*[10]—A solution of compound (**8**) (12 mg) in dioxane (2.5 ml) containing 1.5M HCl (2.5 ml) was kept overnight at room temperature. The reaction mixture was treated in the usual manner and the residue was subjected repeatedly to preparative TLC (benzene–acetone, 3:1 and isopropyl ether–acetone, 10:1) to yield chlorohydrin (**5a**), murralongin (**3**), minumicrolin (**7a**), and murrangatin (**6a**) in 25, 17, 8, and 50% yield, respectively. Subsequently, compound (**5a**) (7 mg) in dioxane (2.5 ml) was further treated with 1.5M HCl (2.5 ml) at room temperature for 36 h. The reaction mixture was treated with water, neutralized with aqueous $NaHCO_3$ and then extracted with CH_2Cl_2. The

organic extracts were dried (anhydrous $MgSO_4$), and concentrated to dryness under reduced pressure. The residue was subjected to preparative TLC (silica gel, isopropyl ether–acetone, 10:1) to yield murralongin (**3**) (2 mg) and murrangatin (**6a**) (3 mg). Murrangatin (**6a**) was isolated as colourless prisms; m.p. 116 °C ether); $[\alpha]_D$ −10° (*c* 0.29 in $CHCl_3$); λ_{max} 248, 258, and 321 nm; λ_{max} 3 500 (OH), 1 730 (CO), and 1 605 cm^{-1} (C=C); δ_H: see Table; *m/z* (CI) 294 $[M + NH_4]^+$; *m/z* (CE) 206, 205 (100%), 191, and 175. The ^1H NMR spectrum [in $CDCl_3$ with added chiral shift reagent Eu(hfc)$_3$] of murrangatin (**6a**) isolated from this plant material was shown to be a 3:1 mixture of enantiomers.

Murrangatin Isovalerate (**6b**).—This was isolated as colourless prisms; m.p. 100–103 °C (ether); $[\alpha]_D$ −2.97 (*c* 0.10 in $CHCl_3$); λ_{max} 247, 257, and 321 nm; ν_{max} 1 735 (CO) and 1 610 cm^{-1} (C=C); δ_H: see Table; δ_C 172.98 (s), 160.29 (s), 159.96 (s), 152.77 (s), 143.59 (d), 141.00 (s), 128.69 (d), 116.18 (s), 116.02 (s), 114.72 (t), 113.54 (d), 113.11 (s), 107.77 (d), 79.24 (d), 68.32 (d), 56.32 (q), 43.67 (t), 25.70 (q), 22.45 (2 q), and 15.62 (q); *m/z* (CI) 378 $[M + NH_4]^+$ and 361 $[M + H]^+$; *m/z* (EI) 289, 275, 259, 206 (14%), 205 (100), and 175.

Esterification of Murrangatin (**6a**).—A solution (0.3 ml) of isovaleryl chloride (50 mg) in tetrahydrofuran (THF) (1 ml) was added to a solution of compound (**6a**) (10 mg) in pyridine (1 ml) and the mixture was stirred for 2 h at room temperature. The solvent was evaporated under reduced pressure and the residue was separated by preparative TLC (silica gel, isopropyl ether–acetone, 10:1) to yield compounds (**6b**) (2 mg) (**6c**) (4 mg), and (**6a**) (5 mg). A product (**6b**) was found to be identical with murrangatin isovalerate isolated from the plant, as confirmed by UV ^1H NMR, and IR spectroscopic comparisons. Compound (**6c**); λ_{max} 248, 258, 311sh, and 322 nm; ν_{max} 3 500 (br, OH), 1 730 (CO), and 1 610 cm^{-1} (C=C); δ_H: see Table; *m/z* (EI) 290, 259, 258, 231, 206, 205, 189, and 175.

Murrangatin Acetonide (**6e**).—A solution of murrangatin (**6a**) (7 mg) in acetone (10 ml) and a catalytic amount of *p*-TsOH were stirred for 6 h at room temperature. The mixture was then neutralized with $NaHCO_3$ and the solvent was evaporated under reduced pressure. The residue was subjected to silica gel preparative TLC to yield compound (**6e**) (7 mg) as colourless prisms, m.p. 113–115 °C (ether); λ_{max} 249, 258, and 320 nm; ν_{max} 1 730 (CO) and 1 605 cm^{-1} (C=C); δ_H 1.55 (3 H, s, Me), 1.70 (3 H, s, Me), 1.74 (3 H, s, 3′-Me), 3.93 (3 H, s, OMe), 4.85 (1 H, s, C=CH_2), 4.96 (1 H, s, C=CH_2), 5.01 (1 H, d, *J* 9.1 Hz, 2′-H), 5.57 (1 H, d, *J* 9.1 Hz, 1′-H), 6.26 (1 H, d, *J* 9.4 Hz), 6.87 (1 H, d, *J* 8.7 Hz, 6-H), 7.41 (1 H, d, *J* 8.7 Hz, 5-H), and 7.60 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (EI) 316 (M^+), 301, 259, 246 (100%), 231, 205, 203, 189, and 175 (Found: M^+, 316.1348. Calc. for $C_{18}H_{20}O_5$: M^+, 316.1310).

Minumicrolin (**7a**).—This was isolated as colourless prisms; m.p. 129–132 °C (ether); $[\alpha]_D$ +29° (*c* 0.31 in $CHCl_3$); λ_{max} 248, 258, and 320 nm; ν_{max} 3 500 (OH), 1 730 (CO), and 1 608 cm^{-1} (C=C); δ_H: see Table; *m/z* (CI) 294 $[M + NH_4]^+$; *m/z* (EI) 206, 205 (100%), 191, and 175. The ^1H NMR spectrum [in $CDCl_3$, containing the chiral shift reagent Eu(hfc)$_3$] of minumicrolin (**7a**) obtained from this plant material was shown to contain no enantiomer.

Minumicrolin Isovalerate (**7b**).—This was isolated as a colourless oil; $[\alpha]_D$ +40.9° (*c* 0.086 in $CHCl_3$); λ_{max} 248, 258, and 324 nm; ν_{max} 3 500 (OH), 1 730 (CO), and 1 610 cm^{-1} (C=C); δ_H: see Table; *m/z* (CI) 378 $[M + NH_4]^+$ and 361 $[M + H]^+$; *m/z* (EI) 289, 245, 206 (13%), 205 (100), 189, 175 (11), 162, and 147.

Esterification of Minumicrolin (**7a**).—A solution (0.3 ml) of isovaleryl chloride (50 mg) in THF (1 ml) was added to a solution of compound (**7a**) (9 mg) in pyridine and the mixture was stirred for 40 min at room temperature. Following further addition of the solution of isovaleryl chloride (0.3 and 0.2 ml in THF, respectively) at intervals of 20 min, the reaction mixture was stirred for a further 20 min and then concentrated. The residue was subjected to silica gel preparative TLC to afford compounds (**7b**) (1 mg), (**7c**) (5 mg), and (**7d**) (6 mg). A product (**7b**) was found to be identical with natural minumicrolin isovalerate by comparison with UV, IR and ^1H NMR spectra. *Compound* (**7c**): λ_{max} 248, 258, and 320 nm; ν_{max} 3 500 (br OH), 1 730 (CO), and 1 610 cm^{-1} (C=C); δ_H: see Table; *m/z* (EI) 290 (7), 258, 231, 205 (100), 189, and 175. *Compound* (**7d**): Colourless oil; λ_{max} 248, 258, and 321 nm; ν_{max} 1 730 (CO) and 1 610 cm^{-1} (C=C); δ_H: see Table; *m/z* (EI) 344, 290, 259, 231, 206, 205 (100), 189, and 175.

Minumicroline Acetonide (**7e**).—Compound (**7a**) (6 mg) was treated with acetone and *p*-TsOH under the same conditions as for (**6a**) to yield compound (**7e**) (5 mg) as a colourless oil, λ_{max} 250, 259, and 320 nm; ν_{max} 1 730 (CO) and 1 605 cm^{-1} (C=C); δ_H 1.31 (3 H, s, Me), 1.50 (3 H, s, Me), 1.80 (3 H, s, 3′-Me), 3.87 (3 H, s, OMe), 4.63 (1 H, s, C=CH_2), 4.97 (1 H, d, *J* 8.4 Hz, 2′-H), 5.17 (1 H, s, C=CH_2) 6.11 (1 H, d, *J* 8.4 Hz, 1′-H), 6.21 (1 H, d, *J* 9.4 Hz, 3-H), 6.80 (1 H, d, *J* 8.7 Hz, 6-H), 7.35 (1 H, d, *J* 8.7 Hz, 5-H), and 7.57 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (EI) 316 (M^+), 301, 259, 258, 246 (100), and 231 (Found: M^+, 316.1333. Calc. for $C_{18}H_{20}O_5$: M^+, 316.1310).

Catalytic Hydrogenation of Murrangatin (**6a**).—In the presence of a catalytic amount of PtO_2, an ethanolic solution (4 ml) of compound (**6a**) (8 mg) was stirred under hydrogen for 6.5 h at room temperature. The solution was filtered and the filtrate was concentrated under reduced pressure. The residue was subjected to silica gel preparative TLC (benzene–acetone, 3:1) to yield compound (**16a**) as a colourless oil, along with a small amount of compound (**17**). Compound (**16a**): λ_{max} 216 and 282 nm; ν_{max} 1 770 (CO) and 3 300 cm^{-1} (OH); δ_H 0.97 (6 H, d, *J* 6.7 Hz, 3′-Me$_2$), 1.50 (1 H, m, 3′-H), 2.75 (1 H, dd, *J* 5.4 and 8.1 Hz), 2.94 (2 H, dd, *J* 5.4 and 8.1 Hz), 3.75 (1 H, m), 3.87 (3 H, s, OMe), 5.10 (1 H, d, *J* 7.4 Hz, 2′-H), 6.68 (1 H, d, *J* 8.4 Hz, 6-H), and 7.09 (1 H, d, *J* 8.4 Hz, 5-H).

Tetrahydromurrangatin Dibenzoate (**16b**).—A solution of compound (**16a**) (5 mg) in pyridine (4 ml) together with benzoyl chloride (20 mg) was allowed to stand overnight, and the mixture was then concentrated under reduced pressure. The residue was purified by silica gel preparative TLC to afford compound (**16b**) (1.7 mg) as a colourless oil; λ_{max} 204 (ε 28 800 $dm^3\ mol^{-1}\ cm^{-1}$), 227 (18 700), and 275 (2 700); ν_{max} 1 720 cm^{-1} (CO); δ_H 1.00 (3 H, d, *J* 6.7 Hz, 3′-Me), 1.06 (3 H, d, *J* 6.7 Hz, 3′-Me), 1.91 (1 H, m, 3′-H), 2.50–3.00 (4 H, m, 3′,4′-H$_2$), 3.91 (3 H, s, OMe), 6.12 (1 H, dd, *J* 7.4 and 4.0 Hz, 2′-H), 6.65 (1 H, d, *J* 8.4 Hz, 6-H), 6.78 (1 H, d, *J* 7.4 Hz, 1′-H), 7.07 (1 H, d, *J* 8.4 Hz, 5-H), 7.20–7.50 (6 H, m), and 8.02 (4 H, m); *m/z* (EI) 488 (M^+, 1.5), 301 (65), 296 (100), 276 (46), 221 (25), 216 (25), 203 (18), and 191 (55); CD (MeOH containing 25% enantiomer): $[\theta]_{234}$ −1 980; $[\theta]_{277}$ 0; and $[\theta]_{220}$ +1 890.

Phebalosin (**8**).[9]—This was isolated as colourless needles; m.p. 118–120 °C (ether); $[\alpha]_D$ −2.8° (*c* 0.47 in $CHCl_3$); λ_{max} 246, 256, and 320 nm; ν_{max} 1 732 (CO) and 1 608 cm^{-1} (C=C); δ_H 1.87 (3 H, s, 3′-Me), 3.92 (1 H, d, *J* 2.0 Hz, 2′-H), 3.97 (3 H, s, OMe), 3.99 (1 H, d, *J* 2.0 Hz, 1′-H), 5.08 (1 H, s, C=CH_2), 5.30 (1 H, s, C=CH_2), 6.26 (1 H, d, *J* 9.4 Hz, 3-H), 6.87 (1 H, d, *J* 8.7 Hz, 6-H), 7.41 (1 H, d, *J* 8.7 Hz, 5-H), and 7.61 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (EI) 258

(M^+, 69%), 229 (41), 213 (59), 199 (55), 189 (100), 175 (45), 160 (47), and 131 (55).

Osthol (**9**).[13]—This was isolated as colourless prisms; m.p. 79–81 °C (ether); λ_{max} 249, 258, and 322 nm; ν_{max} 1 720 (CO) and 1 610 cm^{-1} (C=C); δ_H 1.67 (3 H, s), 1.84 (3 H, s, 3′-Me), 3.53 (2 H, d, *J* 7.4 Hz, 1′-H), 3.92 (3 H, s, OMe), 5.22 (1 H, t, *J* 7.4 Hz, 2′-H), 6.23 (1 H, d, *J* 9.4 Hz, 3-H), 6.83 (1 H, d, *J* 8.7 Hz, 6-H), 7.29 (1 H, d, *J* 8.7 Hz, 5-H), and 7.61 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (EI) 244 (M^+, 100), 229 (38), 213 (23), 201 (28), and 189 (38).

Mexoticin (**10**).[15]—This was isolated as colourless prisms; m.p. 186–188 °C (ether); $[\alpha]_D$ −2.94° (*c* 3.37 in $CHCl_3$); λ_{max} 222sh, 238, 254sh, 260, 311, 321, 333, 340, and 348sh nm; ν_{max} 3 500 (OH), 1 710 (CO), and 1 600 cm^{-1} (C=C); δ_H 1.31 (3 H, s, 3′-Me), 1.32 (3 H, s, 3′-Me), 2.55 (2 H, s, OH), 2.88 (1 H, dd, *J* 10.1, 14.1 Hz, 1′-H), 2.99 (1 H, dd, *J* 2.7, 14.1 Hz, 1′-H), 3.59 (1 H, d, *J* 8.1 Hz, 2′-H), 3.94 (6 H, s, 2 OMe), 6.12 (1 H, d, *J* 9.4 Hz, 3-H), 6.34 (1 H, s, 6-H), and 7.98 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (CI) 326 $[M + NH_4]^+$; *m/z* (EI) 250 (13%), 249 (15), 245 (13), 219 (55), 207 (68), 189 (34), 177 (100), 161 (23), 147 (14), and 131 (31).

Sibiricin (**11**).[16]—This was isolated as colourless prisms; m.p. 146–148 °C (ether); $[\alpha]_D$ −49.4° (*c* 0.36 in $CHCl_3$); λ_{max} 224sh, 240, 252, 260, and 326 nm; ν_{max} 1 720 (CO), 1 620, and 1 600 cm^{-1} (C=C); δ_H 1.28 (3 H, s, 3′-Me), 1.48 (3 H, s, 3′-Me), 2.85–3.20 (3 H, m, 1′, 2′-H), 3.94 (6 H, s, 2 OMe), 6.15 (1 H, d, *J* 9.4 Hz, 3-H), 6.34 (1 H, s, 6-H), and 8.00 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (EI) 290 (M^+, 49%), 247 (96), 232 (57), 219 (100), 217 (72), 189 (53), 161 (55), and 149 (57).

Coumurrayin (**12**).[17]—This was isolated as colourless prisms; m.p. 154–156 °C (ether); λ_{max} 252sh, 260, and 325 nm; ν_{max} 1 720 and 1 600 cm^{-1}; δ_H 1.65 (3 H, s, 3′-Me), 1.80 (3 H, s, 3′-Me), 3.42 (2 H, d, *J* 8.0 Hz, 1′-H), 3.89 (6 H, s, 2 OMe), 5.16 (1 H, t, *J* 8.0 Hz, 2′-H), 6.09 (1 H, d, *J* 10.0 Hz, 3-H), 6.28 (1 H, s, 6-H), and 7.93 (1 H, d, *J* 10.0 Hz, 4-H); *m/z* (EI) 274 (M^+, 65%), 259 (100), 244 (44), 231 (29), 229 (37), 219 (19), and 206 (19).

Sibirinol (**13**).[18]—This was isolated as a colourless oil; $[\alpha]_D$ −0.5° (*c* 0.41 in $CHCl_3$); λ_{max} 261 and 324 nm; ν_{max} 1 720 (CO) and 1 600 cm^{-1} (C=C); δ_H 1.88 (3 H, s, 3′-Me), 2.04 (1 H, s, OH), 2.99 (1 H, dd, *J* 8.4, 13.8 Hz, 1′-H), 3.11 (1 H, dd, *J* 4.7, 13.8 Hz, 1′-H), 3.94 (6 H, s, 2 OMe), 4.31 (1 H, m, 2′-H), 4.80 (1 H, s, C=CH_2), 4.90 (1 H, s, C=CH_2), 6.15 (1 H, d, *J* 10.0 Hz, 3-H), 6.34 (1 H, s, 6-H), and 7.99 (1 H, d, *J* 10.0 Hz, 4-H); *m/z* (EI) 290 (M^+, 1%), 275, 220 (54), 219 (100), 205 (17), 175, 161 (46), 146, and 131 (11).

6-*Methoxy-7-geranyloxycoumarin* (**14**).[19]—This was isolated as colourless prisms; m.p. 81–83 °C (ether); λ_{max} 229, 259, 296, and 344 nm; ν_{max} 1 720 (CO) and 1 610 cm^{-1} (C=C); δ_H 1.59 (3 H, s, Me), 1.77 (3 H, s, Me), 1.65 (3 H, s, Me), 2.10 (4 H, m), 3.91 (3 H, s, OMe), 4.69 (2 H, d, *J* 6.4 Hz), 5.07 (1 H, m), 5.48 (1 H, t, *J* 6.4 Hz), 6.28 (1 H, d, *J* 10.0 Hz, 3-H), 6.83 (1 H, s, 5 or 8-H), 6.85 (1 H, s, 8 or 5-H), and 7.62 (1 H, d, *J* 10.0 Hz, 4-H); *m/z* (CI) 346 $[M + NH_4]^+$ and 329 $[M + H]^+$; *m/z* (EI) 193, 192 (100%), 177, 164, 149, 137, and 136.

Umbelliferone (**15**).[14]—This was isolated as colourless prisms; m.p. 223–225 °C (acetone); λ_{max} 216, 245sh, 258sh, 279, and 322 nm; ν_{max} 3 300, 1 730, 1 710 (CO), and 1 610 cm^{-1} (C=C); δ_H([$^2H_6$]-acetone) 6.16 (1 H, d, *J* 9.4 Hz, 3-H), 6.75 (1 H, d, *J* 2.4 Hz, 8-H), 6.84 (1 H, dd, *J* 2.4, 8.7 Hz, 6-H), 7.51 (1 H, d, *J* 8.7 Hz, 5-H), and 7.87 (1 H, d, *J* 9.4 Hz, 4-H); *m/z* (EI) 162 (M^+, 60%), 134 (100), and 105 (26).

Paniculol (**18**).—This was isolated as a colourless oil; $[\alpha]_D$ +11° (*c* 0.30 in $CHCl_3$); λ_{max} 223, 274, 282, and 291 nm; ν_{max} 3 480 cm^{-1} (OH); δ_H 1.02 (3 H, d, *J* 7.0 Hz), 1.50–2.00 (3 H, overlapped m), 2.60–2.90 (2 H, overlapped m), 3.40–3.60 (2 H, overlapped m), 6.97 (1 H, d, *J* 1.0 Hz), 7.11 (1 H, dt, *J* 8.0, 1.5 Hz), 7.18 (1 H, dt, *J* 8.0, 1.5 Hz), 7.34 (1 H, d, *J* 8.0 Hz), 7.60 (1 H, d, *J* 8.0 Hz), and 7.93 (1 H, br s, NH); *m/z* (EI) 203 (M^+, 15%), 160, 131 (21), and 130 (100) (Found: M^+, 203.1297. Calc. for $C_{13}H_{17}NO$: M^+, 203.1309).

Reduction of Paniculidine-A (**19**) *with* $LiAlH_4$.—A solution of compound (**19**) (8 mg) in dry ether (10 ml) was added dropwise to a solution of $LiAlH_4$ (80 mg) in dry ether (30 ml) in an ice-bath and the mixture was stirred for 1 h at room temperature. A few drops of ice–water were added and the mixture was filtered. The filtrate was extracted with ether. The extract was dried (anhydrous $MgSO_4$) and concentrated to give a colourless syrup (7 mg), which was found to be identical (IR, ^1H NMR, and mass spectroscopy) with paniculol (**18**) isolated from the natural plant.

Paniculidine-A (**19**).[6a]—This was isolated as a pale yellow syrup; $[\alpha]_D$ −10.8° (*c* 0.43 in $CHCl_3$); λ_{max} 222, 277sh, 282, and 291 nm; ν_{max} 3 480 (OH) and 1 730 cm^{-1} (CO); δ_H 1.21 (3 H, d, *J* 7.1 Hz), 1.75 (1 H, br m), 2.10 (1 H, br m), 2.55 (1 H, br m), 2.77 (2 H, d, *J* 7.7 Hz), 3.67 (3 H, s), 6.98 (1 H, s), 7.11 (1 H, t, *J* 7.7 Hz), 7.19 (1 H, t, *J* 7.7 Hz), 7.35 (1 H, d, *J* 7.7 Hz), 7.60 (1 H, d, *J* 7.7 Hz), and 7.93 (1 H, br s, NH); *m/z* (EI) 231 (M^+, 52%), 200 (12), 143 (36), and 130 (100).

3-*Prenylindole* (**20**).[20]—This was isolated as a pale yellow syrup; λ_{max} 213sh, 224, 258, 282, and 291 nm; ν_{max} 3 480 cm^{-1} (NH); δ_H 1.75 (3 H, s), 1.76 (3 H, s), 3.45 (2 H, d, *J* 7.1 Hz), 5.44 (1 H, t, *J* 7.1 Hz), 6.94 (1 H, s), 7.10 (1 H, t, *J* 7.7 Hz), 7.18 (1 H, t, *J* 7.7 Hz), 7.34 (1 H, d, *J* 7.7 Hz), 7.59 (1 H, d, *J* 7.7 Hz), and 7.88 (1 H, br s, NH); *m/z* (EI) 185 (M^+, 100%), 170 (68), 155 (23), 143 (19), 130 (40), and 117 (39) (Found: M^+, 185.1200. Calc. for $C_{13}H_{15}N$: M^+, 185.1202).

Yuehchukene (**21**).[5b]—This was isolated as a colourless oil; λ_{max} 223sh, 282, and 290sh nm; ν_{max} 3 475 cm^{-1} (NH); δ_H 0.86 (3 H, s), 1.09 (3 H, s), 1.55 (1 H, m), 1.65 (3 H, s), 2.26 (1 H, d, *J* 7.8 Hz), 3.16 (1 H, t, *J* 8.1 Hz), 4.01 (1 H, m), 4.56 (1 H, d, *J* 8.1 Hz), 5.69 (1 H, br s), 7.26–6.97 (6 H, overlapped m), 7.38 (1 H, d, *J* 7.4 Hz), 7.44 (1 H, d, *J* 7.4 Hz), 7.49 (1 H, br s), 7.56 (1 H, d, *J* 7.4 Hz), and 8.02 (1 H, br s); *m/z* (EI) 366 (M^+, 100%), 351 (60), 269 (10), 257 (21), 234 (33), and 130 (33) (Found: M^+, 366,2101. Calc for $C_{26}H_{26}N_2$: M^+, 366.2095.

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