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BIOTRANSFORMATION OF (−)-*CIS*-MYRTANOL AND (+)-*TRANS*-MYRTANOL BY PLANT PATHOGENIC FUNGUS, *GLOMERELLA CINGULATA*

MITSUO MIYAZAWA,* YASUHIRO SUZUKI and HIROMU KAMEOKA

Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae, Higasiosaka-shi, Osaka 577, Japan

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Key Word Index—*Glomerella cingulata*; plant pathogenic fungus; (−)-*cis*-myrtanol; (+)-*trans*-myrtanol; (3*S*)-3-hydroxy-*cis*-myrtanol; 4-oxo-*cis*-myrtanol; (4*R*)-4-hydroxy-*cis*-myrtanol; 5-hydroxy-*cis*-myrtanol; [1*R*, 4*R*, 5*S*]-thujane-7, 10-diol; 3-oxo-*trans*-myrtanol; 9-hydroxy-*trans*-myrtanol; 4-oxo-*trans*-myrtanic acid; 5-hydroxy-*trans*-myrtanic acid; biotransformation.

Abstract—The biotransformation of the diastereoisomers, (−)-*cis*-myrtanol and (+)-*trans*-myrtanol, by *Glomerella cingulata* has been investigated. (−)-*cis*-Myrtanol was initially converted to (3*S*)-3-hydroxy-*cis*-myrtanol, (4*R*)-4-hydroxy-*cis*-myrtanol, 5-hydroxy-*cis*-myrtanol and [1*R*, 4*R*, 5*S*]-thujane-7, 10-diol having the cyclopropane ring. (4*R*)-4-Hydroxy-*cis*-myrtanol was further converted to 4-oxo-*cis*-myrtanol. By comparison (+)-*trans*-myrtanol was converted to 3-oxo-*trans*-myrtanol, 9-hydroxy-*trans*-myrtanol, 4-oxo-*trans*-myrtanic acid and 5-hydroxy-*trans*-myrtanic acid. The structures of the metabolic products were determined by spectral methods.

INTRODUCTION

Terpenoids are widely distributed in the plant kingdom and possesses a range of biological activities. We are interested in derivatization of terpenoids by biotransformation using a plant pathogenic fungus. We have demonstrated the microbial transformation of (+)-cedrol [1], 1,8-cineole [2], (−)-α-bisabolol [3], (−)-globulol [4], (+)-ledol [4], (−)-nopol [5], (+) and (−)-camphorquinones [6], racemic *cis*- and *trans*-linalool oxide-pyranoid [7], karahanaenone [8], (±)-2-methylcyclohexanone [9], (±)-3-methylcyclohexanone [9], 4-methylcyclohexanone [9] by the plant pathogenic fungus, *Glomerella cingulata*.

In this paper, we describe the metabolism of (−)-*cis*-myrtanol (**1**) and (+)-*trans*-myrtanol (**2**) which exhibit activity as an insect repellent for lice [10]. These compounds are diastereomers, and have the same fundamental skeleton of (−)-nopol [5].

RESULTS AND DISCUSSION

The metabolism of the substrates **1** and **2** by *G. cingulata* was followed for 16 days. The substrates and metabolites were detected by TLC and GC analysis which revealed that compounds **1** or **2** were converted to five and four metabolic products, respectively (Figs 1 and 2). In order to determine the structures of the metabolites a large scale 16-day incubation of **1** (4.32 g) with *G. cingulata* was conducted. After incubation, the culture medium was extracted and the metabolites were purified by silica gel chromatography to give compounds **1-1** to **1-5**. The structures of the metabolites were determined from their ^{1}H and ^{13}C NMR, IR and mass spectra. The major compound **1-1** had a molecular formula $C_{10}H_{18}O_2$ as determined from the high resolution mass spectral data of the diacetate **1-1a**. The NMR spectrum showed a hydroxyl group at C-3. In order to determine the absolute configuration of the C-3 secondary hydroxyl group, Mosher's (^{1}H) method was applied [12, 13]. The metabolite **1-1** was esterified with (*R*)- and (*S*)-MTPA, after protection of the hydroxyl group on C-10 by TBDMS, as described in the Experimental [11]. $\Delta\delta$ ($\delta_S-\delta_R$) values for the MTPA ester of **1-1** are given in the Experimental. These results showed that C-3 had the *S*-configuration and therefore **1-1** was identified as (3*S*)-3-hydroxy-*cis*-myrtanol.

The EI-mass spectrum of **1-2** showed $[M]^+$ at *m/z* 168, corresponding to the molecular formula $C_{10}H_{16}O_2$. The IR and ^{13}C NMR spectra showed the presence of a carbonyl group (IR ν_{max}: 1702 cm^{-1}, δ_C 214.0). By comparison with the coupling constant ($J_{2,3}$ = 10.8 Hz) of H-2 of *cis*-verbanone [15], the car-

* Author to whom correspondence should be addressed.

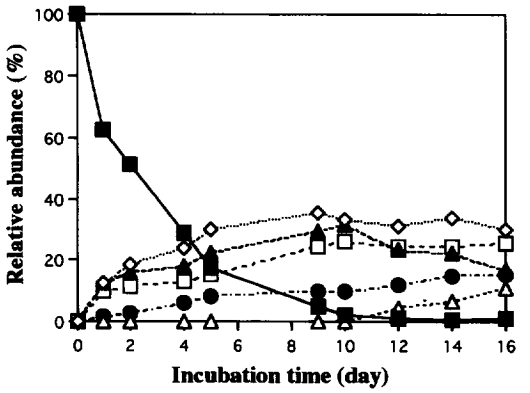


Fig. 1. Biotransformation of (−)-*cis*-myrtanol (**1**) by *G. cingulata*. ■ = (−)-*cis*-myrtanol (**1**), ◇ = (3*S*)-(−)-3-hydroxy-*cis*-myrtanol (**1-1**), △ = (−)-4-oxo-*cis*-myrtanol (**1-2**), ▲ = (4*R*)-(−)-4-hydroxy-*cis*-myrtanol (**1-3**), □ = (−)-5-hydroxy-*cis*-myrtanol (**1-4**), ● = [1*R*, 4*R*, 5*S*]-thujane-7,10-diol (**1-5**).

bonyl group was established to be at the C-4 position. The metabolic product **1-2** was thus identified as to 4-oxo-*cis*-myrtanol.

The compound **1-3** had the molecular formula $C_{10}H_{18}O_2$ based on the HR mass spectrum of diacetate **1-3a**. The NMR spectrum indicated the existence of a hydroxyl group which was located at C-4. The configuration of the introduced hydroxyl group was revealed by the same method as employed with **1-1**. $\Delta\delta$ values are shown in the Experimental and the absolute configuration at C-4 was identified as *R*. Thus, metabolite **1-3** was identified as (4*R*)-4-hydroxy-*cis*-myrtanol. In the course of the metabolism of compounds **1-2** and **1-3**, the increase of **1-2** was related to the decrease of **1-3** (Fig. 1). Therefore, this indicated that **1-2** was the secondary metabolic product formed from **1-3** by *G. cingulata*.

Compound **1-4** had a molecular formula $C_{10}H_{18}O_2$ established by the HR mass spectrum of the diacetate **1-4a**. The ^{1}H NMR and ^{13}C NMR spectra showed the existence of a hydroxyl group which was introduced at C-5. Thus, the metabolite **1-4** was a diol, and it was identified as 5-hydroxy-*cis*-myrtanol.

In the ^{1}H NMR spectrum of **1-5**, the proton signal shifted at δ_H 0.34 and δ_H 0.69, respectively, and they had the same coupling constant (4.8 Hz). In the ^{13}C NMR spectrum, a methylene carbon appeared in high magnetic field (δ_C 11.0). This result indicated that compound **1-5** was composed of a thujane skeleton. The ^{13}C NMR spectrum showed the existence of a primary alcohol and a tertiary alcohol, and the ^{1}H NMR spectrum indicated that they were located at C-10 and C-7. By comparison with 4α-H-thujane-3β-ol [14], the coupling constant (7.5 Hz) between H-3 (β-position) and H-4 of **1-5** established the absolute *R*-configuration of C-4. In addition, the coupling constant (0 Hz) between H-4 and H-5 of **1-5** indicated that the absolute configurations of C-1 and C-5 were *R* and *S*, respectively. Thus, the metabolic product **1-5** was confirmed to be [1*R*, 4*R*, 5*S*]-thujane-7,10-diol.

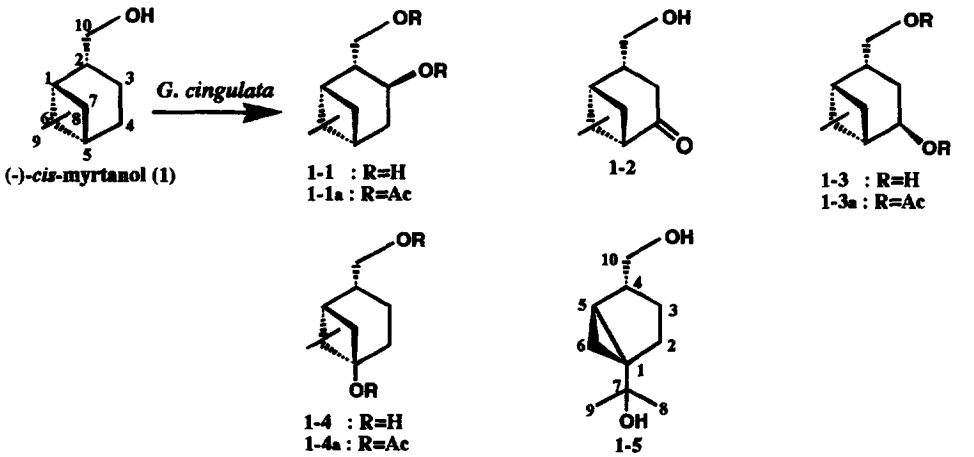
The microbial transformation of **2** was investigated by incubation of **2** (4.00 g) with *G. cingulata* on a large scale for 16 days. After incubation, the culture was extracted as described in the Experimental. Compounds **2-1**–**2-4** were obtained from the extract. The mass spectrum of compound **2-1** showed an ion at *m/z* 168 $[M]^+$. The IR and ^{13}C NMR spectra showed the existence of a carbonyl group (IR ν_{max}: 1706 cm^{-1}, δ_C: 216.0) as a ketone. From the comparison with the ^{13}C NMR signal of **2** and the coupling constant of H-2 of *trans*-pinocamphone [15], the position of the ketone was established at C-3. In the ^{1}H NMR spectrum of **2-1**, the signal of the methylene proton which was adjoining the hydroxy group shifted in the wide range (δ 3.54 and δ 3.90). It seems that this effect was caused by the immovability by intramolecular hydrogen bond between hydroxyl proton and ketone. This result supported the existence of a ketone at C-3. Thus, **2-1** was determined to be 3-oxo-*trans*-myrtanol.

The compound **2-2** had a molecular formula $C_{10}H_{18}O_2$ based on HRMS of the diacetate **2-2a**. The IR spectrum contained a C–O absorption band (1013 cm^{-1}) due to the presence of a primary alcohol. The ^{1}H NMR spectrum indicated the absence of one methyl group and the presence of one hydroxyl group which was located at C-9 by the ^{13}C NMR spectra of **2-2** and **2-2a**. Thus, **2-2** was elucidated to be 9-hydroxy-*trans*-myrtanol.

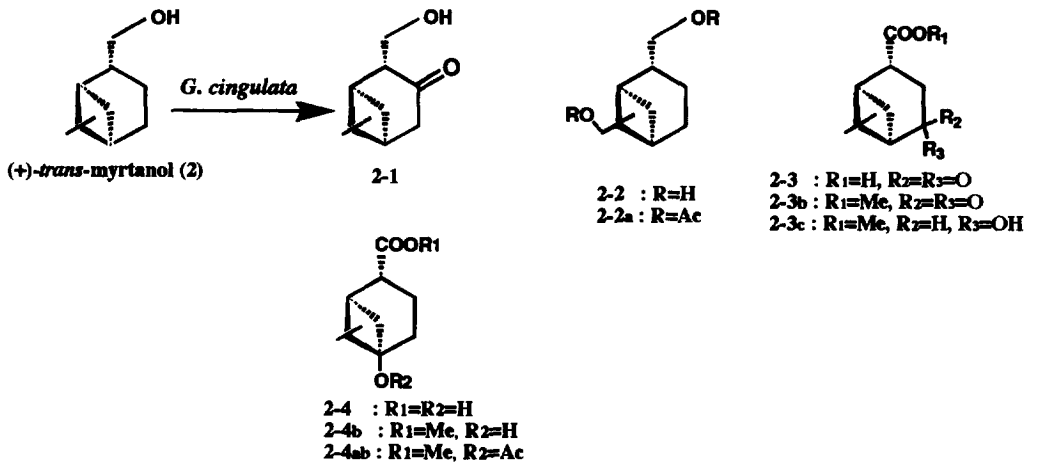
The metabolites from the acidic part were isolated as their methylesters (**2-3b** and **2-4b**) after methylation with diazomethane. The IR and ^{13}C NMR spectra of **2-3b** (molecular formula: $C_{11}H_{16}O_3$ ($[M]^+$ at *m/z* 196)), showed the existence of two carboxyl groups (IR ν_{max}: 1728, 1734 cm^{-1}, δ_C: 211.4, 174.9). In the ^{1}H NMR spectrum there was no signal corresponding to a primary alcohol. Consideration of the DEPT and ^{13}C NMR spectra and the coupling constant of H-2 of **2-3c** showed that **2-3** was a compound in which the C-10 hydroxyl group was oxidized to a carboxylic acid and there was a carbonyl group at C-4. Therefore, metabolite **2-3** was identified as 4-oxo-*trans*-myrtanic acid.

The other methyl ester **2-4b** had the formula $C_{11}H_{18}O_3$ based upon the acetate **2-4ab** which had a molecular formula $C_{13}H_{20}O_4$ determined by FAB-mass spectrometry (*m/z* 241, $[MH]^+$). The IR and ^{13}C NMR spectra of **2-4b** showed the presence of a carboxyl group (IR ν_{max}: 1730 cm^{-1}, δ_C: 176.5) and a hydroxyl group (IR ν_{max}: 3418 cm^{-1} (O–H)). In the ^{1}H NMR spectrum of **2-4b**, the signal corresponding to a primary alcohol of **2** had disappeared. The ^{13}C NMR spectrum supported the existence of a hydroxyl group at C-5 and a carboxyl group at C-10. From these spectra, the metabolite **2-4** was elucidated to be 5-hydroxy-*trans*-myrtanic acid.

The metabolic products produced from **1** and **2** by *G. cingulata* are shown Schemes 1 and 2. The metabolism of **1** and **2** involved oxidations. Both substrates were oxidized at C-3, C-4 and C-5 whereas oxidation at C-9 and C-10 was found only with **2**. A thujane



Scheme 1. The metabolic products of (−)-*cis*-myrtanol (**1**) by *G. cingulata*.



Scheme 2. The metabolic products of (+)-*trans*-myrtanol (**2**) by *G. cingulata*.

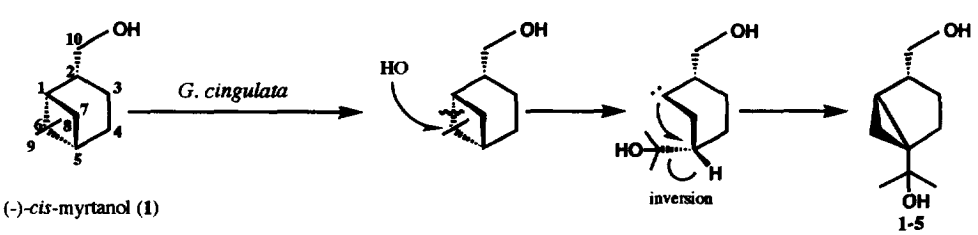
derivative was obtained from **1**; the formation of a thujane from a pinane is very rare (Scheme 3).

With regard to the oxidation at C-10, compound **2** was easily oxidized to a carboxylic acid, but no such oxidation occurred in **1**. Considering the distance between C-10 and the geminal methyl group, the distance in **1** was much longer than that in **2** (Fig. 3.) Therefore, the position of the geminal methyl group had an effect on the specificity of the reaction and this was also seen when a hydroxyl group was introduced into **1-1** and **1-3** as the hydroxyl group introduced faced the *trans*-position of the geminal methyl group. This situation also applied to the production of the metabolite (−)-(4*R*)-4-hydroxynopol from (−)-nopol [5].

EXPERIMENTAL

General. (−)-*cis*-Myrtanol (**1**) and (+)-*trans*-myrtanol (**2**) were purchased from Fluka Chem. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ or CD_3OD with TMS as int. standard at 270.05 and 67.80 MHz, respectively. MS: QP-1000A (Shimazu), 20 eV (ion voltage), 250° (ion source); GC: GC-2D (Shimazu), FID, 1 ml min^{-1} (flow rate), OV-1 (0.25 mm × 25 m), capillary column at 80–240° (2° min^{-1}); TLC: silica gel 60 F_{254} pre-coated (layer thickness 0.25 mm, Merck); C.C.: silica gel developed with *n*-hexane–EtOAc gradient and $CHCl_3$–EtOAc gradient.

Preculture of G. cingulata. Spores of *G. cingulata* (gift from Prof. M. Hyakumachi, Gifu University)



Scheme 3. Probable scheme for the formation of **1-5**.

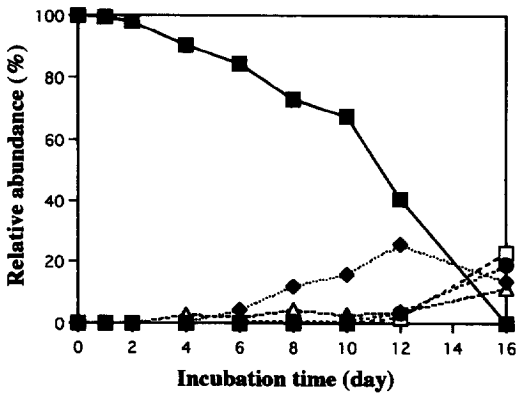


Fig. 2. Biotransformation of (+)-*trans*-myrtanol (**2**) by *G. cingulata*. ■ = (+)-*trans*-myrtanol (**2**), ◆ = (+)-3-oxo-*trans*-myrtanol (**2-1**), △ = (+)-9-hydroxy-*trans*-myrtanol (**2-2**), □ = (+)-4-oxo-*trans*-myrtanic acid (**2-3**), ● = (+)-5-hydroxy-*trans*-myrtanic acid (**2-4**).

which had been preserved at low temp were inoculated into sterilized culture medium (sucrose 3.75 g, glucose 3.75 g, polypeptone 1.25 g, $MgSO_4 \cdot 7H_2O$ 0.125 g, KCl 0.125 g, K_2HPO_4 0.25 g, $FeSO_4 \cdot 7H_2O$ 0.0025 g for 250 ml H_2O) in a shaking flask and shaken at 28° for 2 days. The mycelia were then transplanted on to petri dishes which contained 16 ml culture media (pH 7.2) and were incubated at 28° without shaking for 3 days.

Biotransformation of (−)-cis-*myrtanol* (**1**). Compound **1** (4.32 g) was dissolved in 27 ml of EtOH and 100 μl of this soln added per petri dish to the culture medium (it was established that EtOH did not adversely affect **1** or the mycelia). The cultures of *G. cingulata* were incubated under the same conditions as above for 16 days.

Isolation of the metabolic products (**1-1–1-4**). After incubation, the culture media was collected, saturated with NaCl, and extracted with CH_2Cl_2 and EtOAc. The mycelia were also collected and extracted with CH_2Cl_2 for 3 days. Both extracts were combined, and the solvent was evapd under red. press. The extract (4.10 g) was dissolved in CH_2Cl_2 and washed with 5% aq. $NaHCO_3$, and sepd into a neutral (3.00 g) and an acid part (0.25 g).

Biotransformation of (+)-trans-*myrtanol* (**2**). Compound **2** (4.00 g) was dissolved in 25 ml of EtOH and 100 μl of this soln added per a petri dish to the culture medium (EtOH did not adversely affect **3** or the mycelia). The *G. cingulata* cultures were further incubated under the same conditions for 16 days.

Isolation of the metabolic products (**2-1–2-4**). After incubation, the culture media was collected, saturated with NaCl, and extracted with CH_2Cl_2 and EtOAc. The mycelia were also collected and extracted with CH_2Cl_2 for 3 days. Both extracts were combined, and the solvent was evapd under red. press. The extract (4.70 g) was dissolved in CH_2Cl_2 and washed with 5% aq. $NaHCO_3$, and sepd into a neutral (2.10 g) and an acid part (1.87 g).

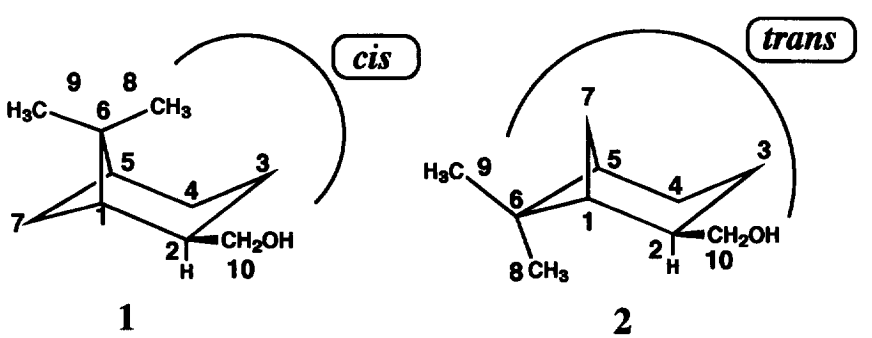
Metabolites from (−)-cis-*myrtanol* (**1**). The neutral fr. (3.00 g) was purified by silica gel CC with hexane–EtOAc and $CHCl_3$–EtOAc gradient repeatedly to give the metabolic products **1-1** (648 g), **1-2** (240 mg), **1-3** (360 mg), **1-4** (552 mg) and **1-5** (336 mg). The R_t on GC and R_f value on TLC were as follows: **1-1** (25.8 min, 0.38), **1-2** (28.6 min, 0.48) **1-3** (28.9 min, 0.32), **1-4** (25.8 min, 0.48), **1-5** (22.2 min, 0.46). *n*-Hexane–EtOAc (1:9) was used as the developing solvent for TLC.

(3S)-3-*Hydroxy*-cis-*myrtanol* (**1-1**). Crystals; mp 62.4–68.5°; $[\alpha]_D^{20}$ +6.79° ($CHCl_3$; *c* 0.45). EIMS *m/z* (rel. int.): 137(3), 134(3), 127(4), 121(7), 91(8), 82(64), 70(base), 55(71), 43(55). IR ν_{max} cm^{-1}: 3362, 2922, 1656, 1471, 1365, 1149, 1085, 1035. ^1H NMR and ^{13}C NMR: see Tables 1 and 5.

3,10-*Diacetate of* **1-1** (**1-1a**). Compound **1-1** (35 mg) was acetylated in the usual manner to yield **1-1a** (40 mg), oil; $[\alpha]_D^{20}$ +17.2° ($CHCl_3$; *c* 1.0): HRMS *m/z*: 194.1287 ($[M-CH_3CO_2H]^+$, calcd for $C_{12}H_{18}O_2$: 194.2750); EIMS *m/z* (rel. int.): 152(4), 135(3), 134(31), 119(32), 91(13), 82(33), 67(7), 43(base). IR ν_{max} cm^{-1}: 2929, 1737, 1471, 1365, 1244, 1152, 1035, 606. ^1H NMR and ^{13}C NMR: see Tables 1 and 5.

4-*Oxo*-cis-*myrtanol* (**1-2**). Crystals; mp 54.0–59.8°; $[\alpha]_D^{20}$ −38.78° ($CHCl_3$; *c* 0.9). EIMS *m/z* (rel. int.): 168 $[M]^+$(3), 153 $[M-CH_3]^+$(3), 137 $[M-CH_2OH]^+$(23), 109(17), 95(52), 83(base), 55(77), 41(24): IR ν_{max} cm^{-1}: 3411, 2943, 1702, 1468, 1248, 1198, 1092, 1039(C–O). ^1H NMR and ^{13}C NMR: see Tables 1 and 5.

(4R)-4-*Hydroxy*-cis-*myrtanol* (**1-3**). Crystals; mp 76.8–82.8°; $[\alpha]_D^{20}$ −16.30° ($CHCl_3$; *c* 1.0). EIMS *m/z* (rel. int.): 155(5), 139(2), 137(4), 121(3), 110(9), 85(base), 69(26), 43(27). IR ν_{max} cm^{-1}: 3326, 2922, 1656, 1471, 1365, 1258, 1046, 1040. ^1H NMR and ^{13}C NMR: see Tables 1 and 5.



1 **2**

Fig. 3. The configuration of (−)-*cis*-(**1**) and (+)-*trans*-myrtanol (**2**).

Table 1. ^{1}H NMR spectral data for (−)-*cis*-myrtanol (**1**) and metabolites and derivatives (δ, TMS, in $CDCl_3$ at 270.05 MHz)

H	**1**	**1-1**	**1-1a**	**1-2**	**1-3**
1	2.02[a] *ddd* (6.5, 4.8, 1.8)	1.89 *dt* (5.5, 5.5, 1.8)	2.01 *dt* (5.8, 5.8, 2.0)	2.39 *ddd* (6.5, 5.0, 2.0)	2.03–2.09 *m*
2	1.85–1.98 *m*	2.13 *ddt* (10.0, 5.5, 5.5, 1.8)	2.41 *ddt* (8.0, 8.0, 5.5, 2.0)	2.49 *ddddd* (10.5, 8.0, 7.5, 5.5, 2.0)	2.34 *dddt* (11.0, 7.5, 7.5, 6.0, 2.0)
3	1.46 *m*	4.33 *dt* (10.0, 5.5, 5.0)	5.16 *ddd* (9.5, 5.5, 4.5)	2.27 *dd* (20.0, 5.5)	1.88 *ddd* (16.0, 11.0, 2.5)
	1.85–1.98 *m*	—	—	2.81 *ddd* (20.0, 10.5, 2.0)	2.03 *ddd* (16.0, 8.5, 6.0)
4	1.85–1.98 *m*	1.76 *ddd* (13.5, 5.0, 2.2)	1.70 *ddd* (15.0, 4.5, 2.8)	—	4.31 *m*
	2.25 *dddd* (14.0, 9.8, 7.0, 2.2)	2.52 *dddd* (13.5, 10.0, 3.8, 2.0)	2.63 *dddd* (15.0, 9.5, 3.0, 2.4)	—	—
5	1.85–1.98[a] *m*	1.97 *ddt* (5.5, 5.5, 3.8, 2.2)	1.96 *ddt* (5.8, 5.8, 3.0, 2.8)	2.60 *t* (5.5, 5.5)	2.03–2.09 *m*
7a	0.94 *d* (9.5)	1.12 *d* (10.0)	1.13 *d* (10.0)	1.47 *d* (10.5)	1.31 *d* (9.8)
7b	2.38 *ddt* (9.5, 6.5, 6.5, 2.2)	2.44 *ddt* (10.0, 5.5, 5.5, 2.0)	2.44 *ddt* (10.0, 5.8, 5.8, 2.4)	2.67 *dddd* (10.5, 6.5, 5.5, 2.0)	2.26 *ddt* (9.8, 6.0, 6.0, 1.5)
8-Me	0.98 *s*	0.88 *s*	0.95 *s*	0.96 *s*	0.94 *s*
9-Me	1.19 *s*	1.21 *s*	1.23 *s*	1.35 *s*	1.25 *s*
10	3.55 *dd* (10.0, 7.8)	3.64 *dd* (10.0, 5.5)	4.07 *dd* (11.0, 8.0)	3.68 *dd* (10.5, 8.0)	3.53 *dd* (1.05, 7.5)
	3.60 *dd* (10.0, 7.8)	3.72 *dd* (10.0, 10.0)	4.11 *dd* (11.0, 8.0)	3.73 *dd* (10.5, 7.5)	3.58 *dd* (10.5, 7.5)
3-OH	—	1.80–2.60 *br s*	—	—	—
4-OH	—	—	—	—	1.57 *br s*
10--OH	1.36 *br s*	1.80–2.60 *br s*	—	2.27 *br s*	1.57 *br s*
3-OCOMe	—	—	2.02[b] *s*	—	—
10-OCOMe	—	—	2.05[b] *s*	—	—

Coupling constants in Hz.
[a,b] Values are interchangeable within each column.

Table 2. ^{1}H NMR spectral data for (−)-*cis*-myrtanol (**1**) and metabolites and derivatives (δ, TMS, in $CDCl_3$ at 270.05 MHz)

H	**1-3a**	**1-4**	**1-4a**	H	**1-5**
1	2.00–2.18 *m*	1.92–1.97 *m*	1.96–2.38 *m*	2a	1.60 *ddd* (12.0, 9.0, 1.0)
2	2.48 *dddt* (11.0, 8.0, 8.0, 6.0, 2.0)	2.05–2.12 *m*	1.96–2.38 *m*	2b	2.01 *dddd* (12.0, 11.0, 9.0, 1.5)
3	1.90 *ddd* (16.0, 11.0, 2.5)	1.57 *ddt* (13.5, 10.5, 5.5, 5.5)	1.54–1.68 *m*	3a	1.40 *dddd* (13.5, 11.0, 9.0, 7.5)
	2.12 *ddd* (16.0, 9.0, 5.5)	1.90 *ddt* (13.5, 10.5, 3.0, 3.0)	1.96–2.38 *m*	3b	1.56 *ddd* (13.5, 9.0, 1.0)
4	5.25 *m*	1.92–1.97 *m*	1.96–2.38 *m*	4	2.15 *dt* (7.5, 5.0, 5.0)
	—	2.00–2.07 *m*	1.96–2.38 *m*	5	1.19 *dd* (8.5, 4.3)
5	2.00–2.18 *m*	—	—	6a	0.34 *dd* (4.8, 4.3)
7a	1.32 *d* (10.0)	1.42 *d* (9.5)	1.75 *d* (10.0)	6b	0.69 *ddd* (8.5, 4.8, 1.5)
7b	2.29 *ddt* (10.0, 6.0, 6.0, 1.5)	2.30 *ddd* (9.5, 7.5, 2.8)	2.53 *ddd* (10.0, 8.0, 2.3)	8	1.08[c] *s*
8-Me	1.01 *s*	1.02 *s*	1.14 *s*	9	1.29[c] *s*
9-Me	1.25 *s*	1.14 *s*	1.14 *s*	10	3.52 *dd* (10.0, 5.0)
10	3.98 *dd* (10.5, 8.0)	3.55 *dd* (10.5, 7.0)	3.99 *dd* (10.5, 7.5)		3.61 *dd* (10.0, 5.0)
	4.03 *dd* (10.5, 8.0)	3.58 *dd* (10.5, 7.5)	4.03 *dd* (10.5, 8.0)	7-OH	2.14–2.42 *br s*
5-OH	—	1.31 *br s*	—	10-OH	2.14–2.42 *br s*
10-OH	—	1.31 *br s*	—		
4-OCOMe	2.03[a] *s*	—	—		
5-OCOMe	—	—	1.98[b] *s*		
10-OCOMe	2.04[a] *s*	—	2.05[b] *s*		

Coupling constants in Hz.
[a–c] Values are interchangeable within each column.

Table 3. ^{1}H NMR spectral data for (+)-*trans*-myrtanol (**2**) and metabolites and derivatives (δ, TMS, in $CDCl_3$ at 270.05 MHz)

H	**2**	**2-1**	**2-2**	**2-2a**	**2-3**
1	1.90 *ddd* (5.5, 5.0, 1.0)	2.02 *dt* (6.0, 6.0, 2.0)	2.05 *t* (5.5, 5.5)	1.97–2.03 *m*	2.48–2.64 *m*
2	2.16 *m*	2.79 *dddt* (8.5, 5.5, 3.0, 2.0, 2.0)	2.16 *m*	2.31 *m*	2.48–3.14 *m*
3a	1.24 *ddt* (14.5, 10.0, 9.0, 9.0)	—	1.28 *dddd* (14.5, 9.5, 8.8, 8.0)	1.34 *dddd* (14.5, 9.5, 8.0, 8.0)	3.0–3.14[e] *m*
3b	1.62 *ddt* (14.5, 8.5, 8.5, 1.5)	—	1.67 *ddt* (14.0, 9.5, 9.5, 1.5)	1.70 *ddt* (14.5, 9.0, 9.0, 1.5)	2.48–2.64[e] *m*
4	1.74 *dddd* (13.5, 10.0, 3.5, 1.5)	2.69 *ddd* (19.5, 3.0, 2.0)	1.72–1.85 *m*	1.72–1.86 *m*	—
	1.84 *ddddd* (13.5, 9.0, 8.5, 1.2, 1.0)	2.49 *ddd* (19.5, 3.0, 1.3)	1.72–1.85 *m*	1.72–1.86 *m*	—
5	1.89 *dddd* (5.5, 5.0, 3.5, 1.0)	2.13 *tt* (6.0, 6.0, 3.0, 3.0)	2.05 *dt* (5.5, 5.5, 2.0)	1.97–2.03 *m*	2.48–2.64 *m*
7a	1.32 *d* (10.0)	1.18 *d* (11.0)	1.38 *d* (10.0)	1.42 *d* (10.0)	1.79 *d* (10.5)
7b	2.05 *dtt* (10.0, 5.5, 5.5, 1.2, 1.2)	2.51 *dddt* (11.0, 6.0, 6.0, 3.0, 1.3)	2.04–2.13 *m*	2.01–2.12 *m*	2.48–2.64 *m*
8-Me	0.85 *s*	0.93 *s*	0.95 *s*	0.93 *s*	0.91 *s*
9-Me	1.22 *s*	1.36 *s*	—	—	1.40 *s*
9	—	—	3.72[b] *d* (10.5)	4.20[c] *d* (10.5)	—
	—	—	3.78[b] *d* (10.5)	4.24[c] *d* (10.5)	—
10a	3.40 *dd* (10.5, 7.5)	3.54[a] *dt* (11.0, 5.5, 5.5)	3.43 *dd* (10.0, 7.5)	3.87 *dd* (11.0, 7.5)	—
10b	3.44 *dd* (10.5, 6.5)	3.90[a] *dd* (11.0, 8.5)	3.48 *dd* (10.0, 6.5)	3.93 *dd* (11.0, 6.5)	—
9-OH	—	—	not found	—	—
10-OH	not found	2.92 *d* (5.5)	not found	—	—
9-OCOMe	—	—	—	2.04[d] *s*	—
10-OCOMe	—	—	—	2.08[d] *s*	—
COOH	—	—	—	—	not found

Coupling constants in Hz.
[a–c] Values are interchangeable within each column.

Table 4. ^{1}H NMR spectral data for (+)-*trans*-myrtanol (**2**) and metabolites and derivatives (δ, TMS, in $CDCl_3$ and CD_3OD (**2-4**) at 270.05 MHz)

H	**2-3b**	**2-3c**	**2-4**	**2-4b**	**2-4ab**
1	2.47–2.55 *m*	2.23 *ddd* (5.8, 4.8, 1.5)	1.68–2.10 *m*	1.78–2.10 *m*	2.02–2.34 *m*
2	2.47–3.11 *m*	3.08 *dddd* (10.5, 5.5, 2.0, 1.5)	2.73 *t* (8.5, 8.5)	2.77 *t* (8.5, 8.5)	2.81 *t* (8.5, 8.5)
3	3.04–3.11 *m*	1.83 *ddd* (16.0, 10.0, 2.8)	1.68–2.10[a] *m*	1.78–2.10[b] *m*	1.80–1.94[c] *m*
	2.47–2.55 *m*	2.70 *ddd* (16.0, 10.0, 5.5)	1.68–2.10[a] *m*	1.78–2.10[b] *m*	2.02–2.34[c] *m*
4	—	4.36 *ddd* (10.0, 3.5, 2.8)	2.10–2.24[a] *m*	2.17–2.24[b] *m*	2.02–2.34[c] *m*
	—	—	1.68–2.10[a] *m*	1.78–2.10[b] *m*	2.02–2.34[c] *m*
5	2.59 *t* (5.0, 5.0)	2.08 *ddd* (6.0, 4.8, 3.5)	—	—	—
7a	1.79 *dd* (15.0, 5.0)	1.12 *d* (9.5)	1.68–1.98 *m*	1.78–1.95 *m*	2.02–2.34 *m*
7b	2.47–2.55 *m*	2.17 *dddd* (9.5, 6.0, 5.8, 2.0)	1.98–2.10 *m*	1.78–2.10 *m*	2.02–2.34 *m*
8-Me	0.89 *s*	1.12 *s*	0.90 *s*	0.91 *s*	1.02 *s*
9-Me	1.38 *s*	1.26 *s*	1.16 *s*	1.19 *s*	1.18 *s*
4-OH	—	1.72 *s*		—	—
5-OH	—	—	Not found	2.07 *s*	—
5-OCOMe	—	—	—	—	1.98 *s*
COOH	—	—	Not found	—	—
COOMe	3.73 *s*	3.66 *s*	—	3.66 *s*	3.66 *s*

Coupling constants in Hz.
[a–c] Values are interchangeable within each column.

4,10-*Diacetate of* **1-3** (**1-3a**). Compound **1-3** (46 mg) was acetylated in the usual manner to yield **1-3a** (35 mg), oil; $[\alpha]_D^{20}$ −10.13° ($CHCl_3$; *c* 1.0): HRMS *m/z*: 254.1518 ([M]$^+$, calcd for $C_{14}H_{22}O_4$: 254.3278). EIMS *m/z* (rel. int.): 211(1), 195(2), 181(2), 152(4), 151(13), 134(38), 119(28), 105(8), 43(base). IR ν_{max} cm^{-1}: 2943, 1737, 1475, 1369, 1244, 1166, 1035, 978, 603. ^{1}H NMR and ^{13}C NMR: see Tables 2 and 5.

Table 5. ^{13}C NMR spectral data for (−)-*cis*-myrtanol (**1**) and its metabolites and derivatives (67.80 MHz, $CDCl_3$)

C	1	1-1	1-1a	1-2	1-3	1-3a	1-4	1-4a	1-5
1	42.88(*d*)	43.32(*d*)[b]	42.63(*d*)	42.60(*d*)[g]	42.93(*d*)	42.70(*d*)	37.72(*d*)	38.60(*d*)	37.64(*s*)
2	44.43(*d*)	55.38(*d*)	47.85(*d*)	39.75(*d*)[g]	42.57(*d*)	38.25(*d*)	42.53(*d*)	39.72(*d*)	25.14(*t*)[q]
3	18.74(*t*)	68.35(*d*)	68.84(*d*)	36.80(*t*)	27.11(*t*)	27.56(*t*)	20.52(*t*)	20.29(*t*)	27.34(*t*)[q]
4	25.96(*t*)	37.71(*t*)	32.69(*t*)	213.96(*s*)	69.73(*d*)	73.08(*d*)	32.36(*t*)	28.19(*t*)	42.47(*d*)
5	41.45(*d*)	41.82(*d*)[b]	41.14(*d*)	58.20(*d*)	48.39(*d*)	45.06(*d*)	75.87(*s*)	82.43(*s*)	23.37(*d*)
6	38.60(*s*)	38.01(*s*)	37.96(*s*)	40.08(*s*)	38.80(*s*)	38.50(*s*)	43.79(*s*)	43.64(*s*)	11.03(*t*)
7	33.11(*t*)	34.24(*t*)	35.78(*t*)	27.87(*t*)	30.67(*t*)	27.84(*t*)	41.68(*t*)	40.16(*t*)	71.31(*s*)
8	23.28(*q*)[a]	23.91(*q*)[c]	23.70(*q*)[d]	24.63(*q*)[h]	22.79(*q*)[i]	22.82(*q*)[j]	20.52(*q*)[m]	21.48(*q*)[n]	28.09(*q*)[r]
9	27.95(*q*)[a]	27.45(*q*)[c]	27.02(*q*)[d]	26.66(*q*)[h]	27.63(*q*)[i]	27.30(*q*)[j]	22.68(*q*)[m]	23.19(*q*)[n]	27.44(*q*)[r]
10	67.74(*t*)	67.16(*t*)	66.62(*t*)	65.60(*t*)	67.05(*t*)	68.04(*t*)	67.34(*t*)	68.19(*t*)	67.38(*t*)
3-COMe			21.29(*q*)[e]						
3-COMe			170.48(*s*)[f]						
4-COMe						21.35(*q*)[k]			
4-COMe						170.72(*s*)[l]			
5-COMe								21.29(*q*)[o]	
5-COMe								170.09(*s*)[p]	
10-COMe			20.85(*q*)[e]			20.86(*q*)[k]		20.92(*q*)[o]	
10-COMe			171.95(*s*)[f]			171.05(*s*)[l]		171.09(*s*)[p]	

[a–r] Values are interchangeable within each column.

5-*Hydroxy*-cis-*myrtanol* (**1-4**). Crystals; mp 112.4–119.3°; $[\alpha]_D^{20}$ −17.34° ($CHCl_3$; *c* 0.15). EIMS *m/z* (rel. int.): 139(17), 137(4), 121(15), 109(28), 94(22), 83(74), 71(38), 56(22), 43(base). IR ν_{max} cm^{-1}: 3326(O–H), 2943, 1468, 1145, 1092(C–O), 1049(C–O), 1021, 986. ^1H NMR and ^{13}C NMR: see Tables 2 and 5.

5,10-*Diacetate of* **1-4** (**1-4a**). Compound **1-4** (27 mg) was acetylated in the usual manner to yield **1-4a** (22 mg). Oil; $[\alpha]_D^{20}$ −12.89° ($CHCl_3$; *c* 1.0): HRMS *m/z*: 212.1395 ($[M-CH_2CO]^+$, calcd for $C_{12}H_{20}C_3$: 212.2903). EIMS *m/z* (rel. int.): 212(4), 197(1), 196(1), 170(3), 169(5), 152(56), 134(49), 109(46), 43(base). IR ν_{max} cm^{-1}: 2950, 1737, 1471, 1365, 1244, 1074, 1035, 606. ^1H NMR and ^{13}C NMR: see Tables 2 and 5.

[1R, 4R, 5S]-*Thujane*-7,10-*diol* (**1-5**). Oil; $[\alpha]_D^{20}$ −7.45° ($CHCl_3$; *c* 0.35): EIMS *m/z* (rel. int.): 155(2), 152(8), 137(5), 121(22), 109(19), 94(48), 79(59), 59(base), 43(78). IR ν_{max} cm^{-1}: 3355 (O–H), 2929, 1695, 1464, 1372, 1266, 1156, 1046, 929, 737. ^1H NMR and ^{13}C NMR: see Tables 2 and 5.

Preparation of the TBDMS ester of **1-1**. The mixt. of a soln of **1-1** (40 mg) in distilled CH_2Cl_2 (0.47 ml), NEt_3 (0.039 ml), 4-*N*,*N*-dimethylaminopyridine (2.0 mg) and TBDMS-Cl (40 mg) was stirred at room temp for 14 hr. (TBDMS = *tert*-butyldimethylsilyl.) After reaction, the purified TBDMS ester was obtained (46 mg) [11].

Preparation of (R)-(+) *and* (S)-(−)-*MTPA ester of* **1-1**. (*R*)-(+) (71 mg) and (*S*)-(−)-MTPA-Cl (58 mg) were prepd. (MTPA = (*s*)-(−)-α-(trifluoro-methyl) phenylacetic acid) [12]. A soln of the TBDMS ester (23 mg) of **1-1**, (dimethylamino)pyridine (40 mg) and NEt_3 (0.017 ml) in 2.7 ml of distilled CH_2Cl_2 was treated with (*R*)-(71 mg) or (*S*)-MTPA-Cl (58 mg), and the mixt. was stirred at room temp for 12 hr [13]. 3-[(Dimethylamino)propyl]amine (0.020 ml) was added at the end of the reaction and the residue was saturated with NaCl, extracted with CH_2Cl_2, evapd, dried and purified by silica gel CC and PTLC. On account of the loss of the TBDMS group by hydrolysis, each ester (*R*: 45 mg, *S*: 41 mg) was mixed with *n*-Bu_4NF–THF (3 ml) and was stirred at room temp for 1 hr. The residue was saturated with NaCl, extracted with Et_2O, evapd, dried and purified. Consequently, the MTPA ester was yielded (*R*: 21 mg, *S*: 27 mg). $\Delta\delta$ ($\Delta\delta_S - \Delta\delta_R$) values: (C1)proton; 2.03–2.24 = −0.01, (C2)proton; 2.36–2.24 = +0.12, (C3)proton; 5.43–5.41 = +0.02, (C4)proton; 2.66–2.69 = −0.03, 1.76–1.91 = −0.15, (C5)proton; 1.96–2.00 = −0.04, (C7)proton; 2.41–2.42 = −0.01, 1.08–1.11 = −0.03, (C8)methyl; 0.91–0.91 = 0, (C9)methyl; 1.23–1.23 = 0, (C10)proton; 3.60–3.54 = +0.06, 3.79–3.73 = +0.06.

Preparation of the TBDMS ester of **1-3**. The TBDMS ester of **1-3** (30 mg) was obtained (36 mg) in the same manner as that of **1-1** [11].

Preparation of (R)-(+) *and* (S)-(−)-*MTPA esters of* **1-3**. The TBDMS ester (18 mg) of **1-3** was used for the reaction with (*R*)-MTPA-Cl and (*S*)-MTPA-Cl, respectively. The MTPA ester of **1-3** was obtained (*R*: 7 mg, *S*: 9 mg) in the same way as **1-1** [12, 13]. $\Delta\delta$ ($\Delta\delta_S - \Delta\delta_R$) values: (C2)proton; 2.36–2.34 = +0.02, (C3)proton; 2.03–1.92 = +0.11, (C4)proton; 5.54–5.55 = −0.01, (C5)proton; 2.17–2.19 = −0.02, (C7)proton; 1.21–1.29 = −0.08, (C8)methyl; 1.01–1.02 = −0.01, (C9)methyl; 1.26–1.28 = −0.02, (C10)proton; 3.56–3.55 = +0.01, 3.61–3.60 = +0.01.

Metabolites from (+)-trans-*myrtanol* (**2**). The neutral part (2.10 g) was chromatographed over silica gel with a hexane–EtOAc gradient repeatedly to give the metabolic products **2-1** (229 mg) and **2-2** (173 mg). The acidic part (1.87 g) was methylated with CH_2N_2 in the usual manner and the product was purified by

Table 6. ^{13}C NMR spectral data for (+)-*trans*myrtanol (**2**) and its metabolites and derivatives (67.80 MHz, $CDCl_3$, CD_3OD (**2-4**))

C	2	2-1	2-2	2-2a	2-3	2-3b	2-3c	2-4	2-4b	2-4ab
1	42.19(*d*)	40.53(*d*)	37.09(*d*)[c]	38.36(*d*)	38.46(*d*)	38.47(*d*)	40.83(*d*)	40.61(*d*)[k]	38.85(*d*)[n]	39.64(*d*)[q]
2	37.65(*d*)	53.66(*d*)	37.66(*d*)[c]	33.50(*d*)	44.10(*d*)	44.03(*d*)	44.26(*d*)	40.87(*d*)[k]	39.59(*d*)[n]	40.43(*d*)[q]
3	18.14(*t*)	216.26(*s*)	18.27(*t*)	18.18(*t*)	35.17(*t*)	35.46(*t*)	25.02(*t*)[l]	20.17(*t*)	19.19(*t*)	19.26(*t*)
4	24.09(*t*)	44.59(*t*)	23.58(*t*)	23.27(*t*)[d]	211.26(*s*)	211.44(*s*)	71.76(*d*)	31.87(*t*)[l]	30.55(*t*)[o]	26.89(*t*)[r]
5	40.98(*d*)	38.19(*d*)	36.64(*d*)[c]	36.73(*d*)	57.46(*d*)	57.43(*d*)	47.50(*d*)	75.39(*s*)	74.82(*s*)	81.39(*s*)
6	39.16(*s*)	39.77(*s*)	44.81(*s*)	43.06(*s*)	42.11(*s*)	41.98(*s*)	38.18(*s*)	45.46(*s*)	44.64(*s*)	44.64(*s*)
7	23.40(*t*)	29.71(*t*)	23.58(*t*)	23.50(*t*)[d]	23.05(*t*)	22.92(*t*)	28.38(*t*)[l]	33.61(*t*)[l]	33.60(*t*)[o]	31.80(*t*)[r]
8	20.11(*q*)[a]	19.90(*q*)[b]	15.27(*q*)	20.90(*q*)	21.98(*q*)[g]	21.88(*q*)[h]	22.52(*q*)[j]	18.78(*q*)[m]	18.24(*q*)[p]	19.10(*q*)[s]
9	26.62(*q*)[a]	26.12(*q*)[b]	68.97(*t*)	70.33(*t*)	25.77(*q*)[g]	25.71(*q*)[h]	27.10(*q*)[j]	22.15(*q*)[m]	21.10(*q*)[p]	21.74(*q*)[s]
10	66.79(*t*)	63.30(*t*)	66.35(*t*)	67.60(*t*)	179.66(*s*)	174.91(*s*)	176.67(*s*)	179.91(*s*)	176.55(*s*)	176.16(*s*)
5-COMe										21.37(*q*)[s]
5-COMe										169.88(*s*)
9-COMe				15.61(*q*)[f]						
9-COMe				171.55(*s*)[e]						
10-COMe				15.61(*q*)[f]						
10-COMe				171.22(*s*)[e]						
-COOMe						52.16(*q*)	51.75(*q*)		51.67(*q*)	51.70(*q*)

[a–s] Values are interchangeable within each column.

silica gel CC obtain the metabolites **2-3** (416 mg) and **2-4** (274 mg). The R_t in GC and R_f value on TLC were as follows: **2-1** (23.1 min, 0.54), **2-2** (34.4 min, 0.12), **2-3** (36.2 min, 0.12), **2-3b** (– min, 0.72), **2-4** (33.3 min, 0.12), **2-4b** (– min,0.58). The developing solvent for TLC was *n*-hexane–EtOAc (5:5).

3-*Oxo*-trans-*myrtanol* (**2-1**). Oil; $[\alpha]_D^{20}$ +8.40° ($CHCl_3$; *c* 0.4). EIMS *m/z* (rel. int.): 168(2), 153(1), 150(4), 139(1), 137(3), 135(2), 114(26), 82(82), 69(69), 43(base), 41(94). IR ν_{max} cm^{-1}: 3418(O–H), 2936, 1706(C=O), 1471, 1408, 1369, 1323, 1198, 1049(C–O), 1007, 514. ^1H NMR and ^{13}C NMR: see Tables 3 and 6.

9-*Hydroxy*-trans-*myrtanol* (**2-2**). Oil; $[\alpha]_D^{20}$ +20.69° ($CHCl_3$; *c* 1.0). EIMS *m/z* (rel. int.): 139(4), 137(9), 123(12), 122(17), 121(23), 107(23), 93(34), 81(61), 79(42), 55(42), 43(base), 41(36). IR ν_{max} cm^{-1}: 3340, 2929, 1709, 1464, 1379, 1057, 1028, 1014, 936, 634. ^1H NMR and ^{13}C NMR: see Tables 3 and 6.

9,10-*Diacetate of* **2-2** (**2-2a**). Compound **2-2** (29 mg) was acetylated in the usual manner to yield **2-2a** (20 mg). Oil; $[\alpha]_D^{20}$ −13.54° ($CHCl_3$; *c* 1.0): HRMS *m/z*: 212.1389 ($[M-CH_2CO]^+$, calcd for $C_{12}H_{20}O_3$: 212.2903). EIMS *m/z* (rel. int.): 195($[M-OCOCH_3]^+$(9), 152(5), 134(19), 119(24), 93(35), 79(25), 43(base). IRν_{max} cm^{-1}: 2936, 1737, 1461, 1383, 1376, 1237, 1032, 982. ^1H NMR and ^{13}C NMR: see Tables 3 and 6.

4-*Oxo*-trans-*myrtanic acid* (**2-3**). Compound **2-3b** (47 mg) was hydrolyzed with aq. 1% NaOH and treated with a proton ion-exchange resin that had been pretreated with acid. Compound **2-3** (4 mg) was isolated, crystals; mp 172.2–175.8°; $[\alpha]_D^{20}$ +63.63° ($CHCl_3$; *c* 0.2). EIMS *m/z* (rel. int.): 182(4), 167(6), 164(11), 149(7), 137(13), 136(9), 125(4), 121(12), 109(18), 95(36), 83(62), 81(39), 67(34), 55(base), 41(48). IR ν_{max} cm^{-1}: 2957, 2362, 1734, 1681, 1305, 1227, 1198, 1170, 1149, 890, 670. ^1H NMR and ^{13}C NMR: see Tables 3 and 6.

Methyl ester of **2-3** (**2-3b**). Crystals; mp 59.0–62.3°; $[\alpha]_D^{20}$ +47.91° ($CHCl_3$; *c* 1.0): EIMS *m/z* (rel. int.): 196(8), 181(4), 178(8), 164(22), 137(30), 95(65), 83(87), 55(base). IR ν_{max} cm^{-1}: 2957, 1730, 1715, 1436, 1312, 1202, 1174, 1018, 876. ^1H NMR and ^{13}C NMR: see Tables 4 and 6.

Methyl ester of 4-*hydroxy*-trans-*myrtanic acid* (**2-3c**). Compound **2-3b** (40 mg) was reduced with $NaBH_4$ in MeOH. After the reaction, the soln was poured into H_2O, acidified with 1 N HCl and extracted with Et_2O. Compound **2-3c** (40 mg) was isolated as an oil; ^1H NMR and ^{13}C NMR: see Tables 4 and 6.

5-*Hydroxy*-trans-*myrtanic acid* (**2-4**). Compound **2-4b** (34 mg) was treated by the same method as **2-3b**. Compound **2-4** (3 mg) was isolated as crystals; mp 131.1–133.0°. EIMS *m/z* (rel. int.): 166(20), 151(11), 141(17), 138(12), 123(30), 121(41), 105(38), 95(50), 79(76), 67(50), 55(56), 43(base), 41(77). IR ν_{max} cm^{-1}: 3390, 2936, 2525, 2234, 2064, 1702, 1464, 1386, 1333, 1223, 1209, 1124, 975, 627. ^1H NMR and ^{13}C NMR: see Tables 4 and 6.

Methyl ester of **2-4** (**2-4b**). Crystals; mp 49.5–52.5°; $[\alpha]_D^{20}$ +4.56° ($CHCl_3$; *c* 1.0). EIMS *m/z* (rel. int.): 180(2), 167(6), 166(27), 155(21), 148(17), 138(20), 128(17), 123(32), 112(34), 95(48), 81(32), 79(39), 69(36), 55(30), 43(base). IR ν_{max} cm^{-1}: 3418, 2957, 1730, 1432, 1383, 1333, 1202, 1124, 1053, 1039, 1025, 752. ^1H NMR and ^{13}C NMR: see Tables 4 and 6.

Acetate of **2-4b** (**3-4ab**). Compound **2-4b** (53 mg) was acetylated in the usual manner to yield **2-4ab** (58 mg) as an Oil; $[\alpha]_D^{20}$ +4.12° ($CHCl_3$; *c* 1.0). FAB-MS (pos.) *m/z* 241$[MH]^+$. EIMS *m/z* (rel. int.): 209(2), 198(13), 180(13), 166(18), 155(23), 128(13), 121(22), 112(23), 95(20), 79(16), 67(15), 55(21), 43(base), 41(35). IR ν_{max} cm^{-1}: 3454, 2943, 1730, 1457, 1436,

1372, 1337, 1248, 1220, 1174, 1096, 1039, 752, 606. ^{1}H NMR and ^{13}C NMR: see Tables 4 and 6.

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