Tetrahedron 64 (2008) 11193-11197

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

New acylphloroglucinols from the leaves of Rhodomyrtus tomentosa

Asadhawut Hiranrat^a, Wilawan Mahabusarakam^{a,b,*}

^a Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand
^b Natural Products Research Center, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla 90112, Thailand

ARTICLE INFO

Article history: Received 2 July 2008 Received in revised form 5 September 2008 Accepted 18 September 2008 Available online 26 September 2008

Keywords: Rhodomyrtus tomentosa Myrtaceae Rhodomyrtosones A–D Acylphloroglucinol β-Triketone Bisfuran

ABSTRACT

Acylphloroglucinols named rhodomyrtosones A–C and a lepstospermone derivative named rhodomyrtosone D were isolated from the acetone extract of the leaves of *Rhodomyrtus tomentosa* (Aiton) Hassk. together with six known compounds. Their structures were established based on spectroscopic analyses and comparison with related compounds.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Rhodomyrtus tomentosa (Aiton) Hassk. is a flowering plant in the family Myrtaceae and often used in traditional Thai medicine.¹ Extracts and pure compounds from this plant have been shown to inhibit the growth of *Escherichia coli* and *Staphylococcus aureus*.² There have also been reports that it has anti-hepatitis properties.¹ Extracts have also acted as a blood platelet aggregation inhibitor and calcium antagonist.³ In addition, it is used in formulations of skin-whitening, anti-aging and skin-beautifying agents.⁴ Acylphloroglucinol,² flavonoids,^{5,6} tannins⁷ and triterpenes⁸ have been identified from this plant. In the course of our search for bioactive metabolites from plants used in traditional medicine, we are therefore interested in characterizing their chemical constituents. As a part of this project, we have examined the chemical constituents of the leaves of *R. tomentosa* and have isolated four new and six known compounds.

2. Results and discussion

Investigation of the acetone extract of the leaves of *R. tomentosa* resulted in the isolation of four new compounds named rhodomyrtosones A–D (**1–4**) together with six known compounds: rhodomyrtone (**5**),² combretol (**6**),⁶ 3,3',4-tri-O-methylellagic acid (**7**),⁹ endoperoxide G3 (**8**),¹⁰ (6*R*,7*E*,9*R*)-9-hydroxy-4,7-megastigmadien-

* Corresponding author. Tel./fax: +66 7421 2918.

E-mail address: wilawan.m@psu.ac.th (W. Mahabusarakam).

3-one $(9)^{11}$ and α -tocopherol (10). The structures of these compounds were elucidated by analyses of ¹H, ¹³C NMR, COSY, HMQC and HMBC spectroscopic data.

Rhodomyrtosone A(1) was obtained as a white solid. The IR spectrum displayed absorption bands of a hydroxyl (3126 cm^{-1}) . a non-conjugated carbonyl (1720 cm⁻¹) and a conjugated carbonyl (1650 cm⁻¹) group. The HREIMS spectrum showed a molecular ion peak at m/z 456.2133 corresponding to a molecular formula of $C_{26}H_{32}O_7$ with 11 degrees of unsaturation. The ¹³C NMR and DEPT spectra (Table 1) showed 3 carbonyl, 10 quaternary, 4 methine, 1 methylene and 8 methyl carbons. The ¹H NMR spectrum (Table 1) showed resonances of four methyl groups at $\delta_{\rm H}$ 1.52 (H-10), 1.42 (H-11), 1.41 (H-13) and 1.34 (H-12). The evidences for H-12 and H-13 showed HMBC correlations (Table 1) to the carbonyl carbon C-3 (δ_C 211.1) and vinylic oxycarbon C-4a ($\delta_{\rm C}$ 179.7) whereas H-10 and H-11 showed correlations to carbonyl carbons C-1 (δ_C 198.3) and C-3 (δ_C 211.1) indicating the presence of a β -triketone moiety similar to **5**.² The low field chemical shift of C-4a (δ_{C} 179.7) indicated that the β triketone moiety was connected to the oxygen of a furan ring.^{12,13} The signals of the two hydroxyl groups ($\delta_{\rm H}$ 13.27, s, 6-OH and 9.78, s, 8-OH), an aromatic proton ($\delta_{\rm H}$ 6.11, s, H-7) and signals corresponding to an isovaleryl group ($\delta_{\rm H}$ 2.96 and 2.76, dd each, H₂-2'; 2.17, m, H-3'; 1.01, d, H-4' and 0.99, d, H-5') were derived from a di-*C*-substituted phloroglucinol moiety with an isovaleryl group.¹⁴ The spectrum showed further signals of a methine proton ($\delta_{\rm H}$ 4.50, s, H-9) and an isopropyl group ($\delta_{\rm H}$ 2.40, hept, H-2"; 1.11, d, H-3" and 1.09. d. H-4"). The loss of a 43 m/z (C₃H₇) and 85 m/z (C₄H₉CO) from a molecular ion confirmed the presence of isopropyl and isovaleryl





^{0040-4020/\$ -} see front matter \odot 2008 Elsevier Ltd. All rights reserved. doi:10.1016/j.tet.2008.09.054



groups. The HMBC correlations of the methine proton H-9 to C-4a, C-4b, C-8a, C-9a and C-2" as well as of the methyl protons of an isopropyl group to C-1" (δ_C 129.4) provided evidence that the β -triketone was combined to a phloroglucinol moiety via a bisfuran fused-ring bearing the isopropyl group. The 3J HMBC correlations of 6-OH and 8-OH to an aromatic methine carbon C-7 and of 6-OH to C-5 indicated that the aromatic proton was inbetween two hydroxyl groups (C-7), consequently the isovaleryl group was then placed at C-5. The correlations of the methine proton (H-9) to the isopropyl protons in the NOESY experiment provided the assignment of a cis relative stereochemistry. Rhodomyrtosone A was thus identified as 8,10-dihydroxy-5a-isopropyl-2,2,4,4-tetramethyl-7-(3-methylbutyryl)-5a,10b-dihydro-4H-benzo[b]benzo[4,5]furo[3,2-d]-furan-1,3-dione.

Rhodomyrtosone B (**2**) was a yellowish gum. Its molecular ion peak at m/z 442.2352 in the HREIMS spectrum corresponded to a molecular formula of $C_{26}H_{34}O_6$ with 10 degrees of unsaturation. The appearance of the proton resonances (Table 1) of a chelated hydroxyl group (δ_H 13.43, 6-OH), a free hydroxyl group (δ_H 6.40, 8-OH), an aromatic proton (δ_H 6.23, H-7), an isopentyl group (δ_H 4.25, t, H-9; 1.38, obscure, H-1" and H-2"; 0.89, d, H-3" and 0.87, d, H-4", an isovaleryl group (δ_H 3.18 and 2.96, H₂-2'; 2.37, H-3'; 1.04, H-4' and 1.01, H-5') and four singlet methyl groups of a β -triketone moiety (δ_H 1.63, H-12; 1.47, H-13; 1.42, H-11 and 1.39, H-10) as well as its molecular ion of 442.2352 indicated that **2** was a structural

isomer of rhodomyrtone (**5**).² There were slight differences observed for the chemical shifts of the chelated hydroxyl group ($\delta_{\rm H}$ 13.43) and non-equivalent methylene protons of the isovaleryl group ($\delta_{\rm H}$ 3.18 and 2.96), consequently the isovaleryl group was placed at C-5 rather than at C-7. The assignment was fully confirmed by the HMBC experiment (Table 1). Rhodomyrtosone B was therefore identified as 6,8-dihydroxy-9-isobutyl-2,2,4,4-tetramethyl-5-(3-methylbutyryl)-4,9-dihydroxanthene-1,3-dione. It was a 6-demethylated isomer of a synthetic 1,3-dioxo-4,9-dihydro-8-hydroxy-6-methoxy-2,2,4,4-tetramethyl-5-(3-methyl-1-oxobutyl)-9-(2-methylpropyl)-1*H*-xanthene (**11**).¹⁴

Rhodomyrtosone C (**3**) was obtained as a yellowish solid. Its molecular formula of C₄₁H₅₄O₈ was established on the basis of a molecular ion peak at *m*/*z* 674.3853 in its HREIMS spectrum. The ¹H and ¹³C NMR spectra (Table 2) showed the singlet signals that corresponded to two β-triketone moieties [ring A: $\delta_{\rm H}$ 1.64 (H-12), 1.48 (H-13), 1.40 (H-10) and 1.37 (H-11); ring B: $\delta_{\rm H}$ 1.66 (H-14^{*m*}), 1.52 (H-15^{*m*}), 1.44 (H-12^{*m*}) and 1.42 (H-13^{*m*})]. Furthermore, two sets of resonances at $\delta_{\rm H}$ 4.35 (t, H-9), 1.50 (obscure, H-1^{*m*} and H-2^{*m*}), 0.90 (d, H-4^{*m*}) and 0.83 (d, H-3^{*m*}) and at $\delta_{\rm H}$ 4.39 (t, H-7^{*m*}), 1.50 (obscure, H-8^{*m*} and H-9^{*m*}), 0.98 (d, H-11^{*m*}) and 0.84 (d, H-10^{*m*}) were in agreement with the resonances of two isopentyl groups. The remaining resonances were those of an isovaleryl group ($\delta_{\rm H}$ 3.23 and 3.02, dd each, H₂-2'; 2.40, m, H-3'; 1.05, d, H-4' and 1.04, d, H-5') with their carbonyl function

Table 1 The ¹H, ¹³C NMR spectral data and HMBC correlations for rhodomyrtosones A (1) and B (2)

No.	1 ^a				2 ^b		
	δ_{C}^{c}	$\delta_{\rm H}$ (mult., $J_{\rm Hz}$)	HMBC (H \rightarrow C)	δc ^c	$\delta_{ m H}$ (mult., $J_{ m Hz}$)	HMBC (H \rightarrow C)	
1	198.3 s			197.6 s			
2	55.1 s			56.1 s			
3	211.1 s			211.7 s			
4	45.6 s			47.2 s			
4a	179.7 s			166.9 s			
4b	159.8 s			153.3 s			
5	101.7 s			105.9 s			
6	166.7 s			159.0 s			
7	99.6 d	6.11 (s)	C-5, C-6, C-8, C-8a	100.3 d	6.23 (s)	C-5, C-6, C-8, C-8a	
8	159.6 s			159.0 s			
8a	104.2 s			105.9 s			
9	45.0 d	4.50 (s)	C-4a, C-4b, C-8, C-8a, C-9a, C-2″	25.1 d	4.25 (t, 6.0)	C-1, C-4a, C-4b, C-8, C-8a, C-9a, C-1″, C-2″	
9a	113.2 s			114.5 s			
10	24.4 q	1.52 (s)	C-1, C-2, C-3, C-11	24.3 q	1.39 (s)	C-1, C-2, C-3, C-11	
11	24.1 q	1.42 (s)	C-1, C-2, C-3, C-10	24.4 q	1.42 (s)	C-1, C-2, C-3, C-10	
12	23.1 q	1.34 (s)	C-3, C-4, C-4a, C-13	24.8 q	1.63 (s)	C-3, C-4, C-4a, C-13	
13	25.9 q	1.41 (s)	C-3, C-4, C-4a, C-12	25.4 q	1.47 (s)	C-3, C-4, C-4a, C-12	
1′	203.7 s			204.0 s			
2′	51.5 t	2.96 (dd, 14.7, 6.6), 2.76 (dd, 14.7, 6.6)	C-1′, C-3′, C-4′, C-5′	53.6 t	3.18 (dd, 17.0, 6.5), 2.96 (dd, 17.0, 6.5)	C-1′, C-3′, C-4′, C-5′	
3′	25.8 d	2.17 (m, 6.6)	C-2', C-4', C-5'	24.5 d	2.37 (m, 6.5)	C-1', C-2', C-4', C-5'	
4′	22.8 q	1.01 (d, 6.6)	C-2', C-3', C-5'	22.9 q	1.04 (d, 6.5)	C-2', C-3', C-5'	
5′	22.7 q	0.99 (d, 6.6)	C-2', C-3', C-4'	22.6 q	1.01 (d, 6.5)	C-2', C-3', C-4'	
1″	129.4 s			46.9 t	1.38 (obscure)		
2″	35.4 d	2.40 (hept, 6.9)	C-1", C-3", C-4"	24.9 d	1.38 (obscure)		
3″	15.7 q	1.11 (d, 6.9)	C-1", C-2", C-4"	23.4 q	0.89 (d, 6.5)	C-1", C-2", C-4"	
4″	15.6 q	1.09 (d, 6.9)	C-1", C-2", C-3"	23.1 q	0.87 (d, 6.5)	C-1", C-2", C-3"	
6-0H		13.27 (s)	C-5, C-6, C-7		13.43 (s)	C-5, C-6, C-7	
8-0H		9.78 (s)	C-7, C-8		6.40 (br s)		

^a Bruker 300 MHz.

^b Bruker 500 MHz.

^c Multiplicity deduced by DEPT.

forming a hydrogen bonding to the hydroxyl group ($\delta_{\rm H}$ 13.50, 8-OH). Rhodomyrtosone C was therefore identified as 7-hydroxy-8,14-diisobutyl-2,2,4,4,10,10,12,12-octamethyl-6-(3-methylbutyryl)-4,8,12,14-tetrahydro-5,13-dioxapentaphene-1,3,9,11-tetraone. The HMBC correlations confirmed the assigned structure (Table 2).

Rhodomyrtosone D (**4**) was a yellowish solid. The IR spectrum displayed absorption bands of a non-conjugated (1717 cm⁻¹) and a conjugated (1675 cm⁻¹) carbonyl function. The HREIMS spectrum showed a molecular ion peak at m/z 428.2214 corresponding to a molecular formula of C₂₅H₃₂O₆. The ¹³C NMR and DEPT

 Table 2

 The ¹H, ¹³C NMR spectral data and HMBC correlations for rhodomyrtosone C (**3**)^a

No.	δ_{C}^{b}	$\delta_{\rm H}$ (mult., $J_{\rm Hz}$)	HMBC (H \rightarrow C)	No.	δ_{C}^{b}	$\delta_{ m H}$ (mult., $J_{ m Hz}$)	HMBC (H \rightarrow C)
1	197.4 s			1″	45.4 t	1.50 (obscure)	
2	56.0 s			2″	25.3 d	1.50 (obscure)	
3	211.6 s			3″	23.3 q	0.83 (d, 6.0)	C-1", C-2"
4	47.2 s			4″	23.3 q	0.90 (d, 6.0)	C-1", C-2"
4a	166.7 s			1‴	197.6 s		
4b	152.4 s			2‴	56.2 s		
5	105.7 s			3‴	211.4 s		
6	150.5 s			4‴	47.3 s		
7	107.6 s			5‴	166.8 s		
8	160.6 s			6‴	113.5 s		
8a	107.8 s			7‴	25.2 d	4.39 (t, 5.4)	C-4b, C-5, C-6, C-1‴,
							C-5‴, C-6‴, C-8‴, C-9‴
9	25.6 d	4.35 (t, 5.7)	C-1, C-4a, C-4b, C-8,	8‴	46.8 t	1.50 (obscure)	
			C-8a, C-9a, C-1", C-2"				
9a	114.3 s			9‴	25.0 d	1.50 (obscure)	
10	24.9 q	1.40 (s)	C-1, C-2, C-3, C-11	10‴	23.4 q	0.84 (d, 6.0)	C-8‴, C-9‴
11	24.4 q	1.37 (s)	C-1, C-2, C-3, C-10	11 ‴	23.8 q	0.98 (d, 6.0)	C-8 ''', C-10 '''
12	24.7 q	1.64 (s)	C-3, C-4, C-4a, C-13	12‴	24.2 q	1.44 (s)	C-1 "", C-2 "", C-3 ""
13	25.0 q	1.48 (s)	C-3, C-4, C-4a, C-12	13‴	23.8 q	1.42 (s)	C-1 "", C-2 "", C-3 ""
1′	204.6 s			14‴	25.3 q	1.66 (s)	C-3 ''', C-4 ''', C-5 '''
2′	53.9 t	3.23 (dd, 17.4, 6.6), 3.02 (dd, 17.4, 6.6)	C-1', C-3', C-4', C-5'	15‴	24.9 q	1.52 (s)	C-3 ''', C-4 ''', C-5 '''
3′	24.5 d	2.40 (<i>m</i> ,6.6)	C-1', C-2', C-4', C-5'	8-0H		13.50 (br s)	C-7, C-8, C-8a
4′	22.8 q	1.05 (d, 6.6)	C-2', C-3', C-5'				
5′	22.6 q	1.04 (d, 6.6)	C-2', C-3', C-4'				

^a Bruker 300 MHz.

^b Multiplicity deduced by DEPT.

Table 3

The ¹H, ¹³C NMR spectral data and HMBC correlations for rhodomyrtosone D (4)

No.	4 ^a				
	δ_{C}^{b}	$\delta_{\rm H}$ (mult., $J_{\rm Hz}$)	HMBC (H \rightarrow C)		
1 (1')	192.4 s				
2 (2')	56.4 s				
3 (3′)	212.1 s				
4 (4')	45.2 s				
5 (5')	175.7 s				
6 (6')	113.0 s				
7 (7′)	25.7 q	1.27 (s)	C-1 (1'), C-2 (2'), C-3 (3'), C-8 (8')		
8 (8')	22.3 q	1.34 (s)	C-1 (1'), C-2 (2'), C-3 (3'), C-7 (7')		
9 (9′)	23.9 q	1.44 (s)	C-3 (3'), C-4 (4'), C-5 (5')		
10 (10')	24.4 q	1.44 (s)	C-3 (3'), C-4 (4'), C-5 (5')		
1″	46.5 d	4.69 (s)	C-5 (5'), C-6 (6'), C-2", C-3"		
2″	128.2 s				
3″	34.4 d	2.37(hept, 6.9)	C-2", C-4", C-5"		
4″, 5″	15.5 q	1.02 (d, 6.9)	C-2", C-3"		

^a Bruker 300 MHz.

^b Multiplicity deduced by DEPT.

techniques (Table 3) showed signals for 4 carbonyl, 9 quaternary, 2 methine and 10 methyl carbons. The ¹H NMR spectrum (Table 3) revealed three singlet signals of methyl groups at $\delta_{\rm H}$ 1.27 (H-7 and H-7'), 1.34 (H-8 and H-8') and 1.44 (H-9, H-10, H-9' and H-10'). In the HMBC experiment (Table 3), these methyl groups correlated to the carbonyl carbons [δ_C 212.1 (2×C=0), 192.4 (2×C=0)] thus indicating the presence of two moieties of a symmetrical β -triketone. The resonances of a methine proton ($\delta_{\rm H}$ 4.69, s, H-1") and an isopropyl group ($\delta_{\rm H}$ 2.37, hept, H-3" and 1.02, d, H-4", H-5"), similar to those in 1, were also observed. Rhodomyrtosone D or compound 4 is therefore 5a-isopropyl-2,2,4,4,7,7,9,9-octamethyl-7,10b-dihydro-4H,5aH-benzo[b]benzo[4,5]furo[3,2-d]furan-1,3,8,10-tetraone. The HMBC correlations (Table 3) of the methine proton H-1" to the C-5(5'), C-6(6') of a β -triketone, to C-2" and C-3" of the isopropyl group along with the down field shift of C-2" (δ_{C} 128.2) confirmed the assigned structure. In addition, it was in good agreement with a molecular formula of $C_{25}H_{32}O_6$ and the ion peaks at m/z 385, 358, 315 and 288 (Fig. 1). In the NOEDIFF spectrum, irradiation at the resonance of the methine proton H-1" resulted in enhancement of the isopropyl protons, indicating its cis stereochemistry.

It has been suggested that rhodomyrtone (5) arises from precursor 12.² Rhodomyrtosone A (1), we suggest, would thus be derived biogenetically from the oxidation of the isobutyl side chain of precursor **12** followed by formation of benzofuran via cyclization and dehydration. Rhodomyrtosone D **(4)**, we suggest, would then arise from a condensation product **(13)** of leptospermone **(14)** and a syncapic acid **(15)** as a consequence of the oxidation and benzofuran formation as suggested for compound **1**.

In conclusion, four new and six known compounds have been isolated from the leaves of *R. tomentosa*. The unique structures of these new compounds consisted of the β -triketone moiety, which is rare in natural products but have been commonly found in the plants of the Myrtaceae family. Although a number of acylphloro-glucinols condensed with a β -triketone moiety have been reported,^{2,13–15} rhodomyrtosone A is the first example with a novel bisfuran fused-ring skeleton and rhodomyrtosone D is a lepstospermone derivative. Future studies will focus on the investigation of the other constituents and their biological activity.

3. Experimental section

3.1. General experimental procedures

Melting points were determined on a Fisher–Johns melting point apparatus and were uncorrected. Optical rotations were measured in CHCl₃ solution on a JASCO P-1020 polarimeter. UV spectra were recorded by a SPECORD S100 spectrophotometer (Analytikjena). The IR spectra were measured with an FTS 165 FT-IR Perkins–Elmer spectrophotometer. The ¹H and ¹³C NMR spectra were recorded in CDCl₃ by an FT-NMR Bruker Avance 300 and 500 MHz spectrometers using TMS as the internal standard. The EIMS and HREIMS mass spectra were obtained from a MAT 95 XL mass spectrometer (Thermofinigan). Column chromatography (CC) and quick column chromatography (QCC) were performed on silica gel 100 and silica gel 60H (Merck), respectively.

3.2. Sample collection and identification

R. tomentosa samples were collected from Singha Nakorn District, Songkhla Province in the southern part of Thailand during February 2007. The voucher specimen (A. Hiranrat 001) was identified by J. Wai and has been deposited in the herbarium of the Department of Biology, Faculty of Science, Prince of Songkla University, Thailand.



Figure 1. Major mass fragmentation patterns of rhodomyrtosone D (4).

The dried ground leaves of R. tomentosa (2.1 kg) were successively extracted at room temperature with CH₂Cl₂, Me₂CO and MeOH. The Me₂CO extract (46.6 g) was fractionated by dissolving in hexane to give soluble (21.4 g) and insoluble (25.2 g) fractions. The soluble fraction was then separated by OCC and eluted with hexane-CH₂Cl₂, CH₂Cl₂, CH₂Cl₂-Me₂CO and Me₂CO gradient solvent systems. The eluted fractions were combined into fractions A-I on the basis of their TLC characteristics. Fraction B (177.6 mg) was subjected to CC and eluted with hexane-CH₂Cl₂ (85:15) to give fractions B1-B3. Fraction B2 (122.7 mg) was further purified by CC using hexane- CH_2Cl_2 (85:15) as an eluent to produce **10** (73.5 mg). Fraction D (1.3 g) was subjected to CC and eluted with a gradient of hexane-CH₂Cl₂ (9:1) to CH₂Cl₂-Me₂CO (95:5) to give fractions D1-D8. Separation of fraction D6 (105.5 mg) on CC after eluting with hexane-CH₂Cl₂ (1:1) gave **1** (14.1 mg). Fraction F (606.0 mg) was subjected to CC and eluted with CH₂Cl₂ and CH₂Cl₂-MeOH gradient to give fractions F1-F7. Fraction F2 (194.8 mg) was rechromatographed using hexane-Me₂CO (97:3) as an eluent to produce **3** (103.9 mg). Fraction F3 (183.6 mg) was further fractionated by CC and eluted with CH₂Cl₂ to give fractions F31-F36. Fraction F33 (138.1 mg) was purified by CC eluting with hexane-Me₂CO (97:3) to give 5 (23.0 mg). Fraction G (2.92 g) was subjected to CC eluting with CH₂Cl₂-MeOH gradient systems to give fractions G1-G3. Fraction G2 (1.13 g) was fractionated by CC eluting with hexane-Me₂CO (9:1) to give fractions G21–G29. Fraction G24 (66.2 mg) was subjected to CC and eluted with hexane-Me₂CO (95:5) to give fractions G241–G245. Compound 6 (4.2 mg) was obtained from fraction G245 (36.9 mg) by crystallization from hexane-Me₂CO (5:1). The mother liquor was further purified by CC eluting with hexane-Me₂CO (95:5) to produce 8 (0.7 mg) and 2 (1.3 mg). Fraction H (1.67 g) was fractionated by CC eluting with hexane-Me₂CO gradient systems to give fractions H1-H6. Compound 7 (15.7 mg) was crystallized from fraction H5 (304.5 mg), using hexane-Me₂CO (5:1) as a solvent. Fraction I (10.0 g) was fractionated by CC and eluted with hexane-Me₂CO with a polarity gradient to give fractions I1-I8. Fraction I4 (126.1 mg) was subjected to CC and eluted with hexane-Me₂CO (95:5) to produce 4 (9.9 mg). Fraction I5 (210.6 mg) was subjected to CC and eluted with hexane-Me₂CO (95:5) to produce 9 (5.5 mg).

3.3.1. Rhodomyrtosone A (1)

A white solid, mp 125–126 °C. $[\alpha]_D^{29}$ –1.1 (*c* 0.80, CHCl₃). UV (CHCl₃) λ_{max} nm (log ε): 270 (4.39), 327 (3.42). IR (CHCl₃) ν_{max} (cm⁻¹): 3126, 2969, 2935, 2874, 1720, 1650, 1617, 1502, 1452, 1303, 1180, 1052. HREIMS *m*/*z* 456.2133 (calcd for C₂₆H₃₂O₇ 456.2148). EIMS *m*/*z* (% rel int.): 456 (M⁺, 61), 441 (33), 414 (20), 399 (100), 372 (17), 247 (40). ¹H and ¹³C NMR spectral data, see Table 1.

3.3.2. Rhodomyrtosone B (2)

A yellowish gum. $[\alpha]_D^{29} - 182.0 (c 0.06, CHCl_3). UV (CHCl_3) \lambda_{max} nm (log <math>\varepsilon$): 292 (3.82), 333 (3.20). IR (CHCl_3) $\nu_{max} (cm^{-1})$: 3372, 2975, 2952, 2868, 1717, 1653, 1622, 1468, 1385, 1256, 1158, 1038. HREIMS *m/z* 442.2352 (calcd for C₂₆H₃₄O₆ 442.2355). EIMS *m/z* (% rel int.): 442 (M⁺, 1), 428 (13), 413 (14), 386 (22), 385 (91), 330 (8), 315 (28),

236 (46), 221 (24), 167 (38), 166 (63), 149 (77), 123 (60), 97 (49), 70 (100), 69 (90). ¹H and ¹³C NMR spectral data, see Table 1.

3.3.3. Rhodomyrtosone C (3)

A yellowish solid, mp 80–81 °C. $[\alpha]_{D}^{29}$ –23.5 (*c* 0.39, CHCl₃). UV (CHCl₃) λ_{max} nm (log ε): 263 (4.15), 306 (4.19), 348 (3.60). IR (CHCl₃) ν_{max} (cm⁻¹): 3423, 2952, 2868, 1717, 1659, 1617, 1594, 1466, 1382, 1362, 1183, 1158, 1038. HREIMS *m*/*z* 674.3853 (calcd for C₄₁H₅₄O₈ 674.3819). EIMS *m*/*z* (% rel int.): 674 (M⁺, 1), 617 (100), 547 (7), 419 (8). ¹H and ¹³C NMR spectral data, see Table 2.

3.3.4. Rhodomyrtosone D (4)

Yellowish crystal, mp 160–162 °C. UV (CHCl₃) λ_{max} nm (log ε): 246 (4.08), 298 (3.24). IR (CHCl₃) ν_{max} (cm⁻¹): 2974, 2935, 2879, 1717, 1675, 1656, 1468, 1398, 1387. HREIMS *m/z* 428.2214 (calcd for C₂₅H₃₂O₆ 428.2199). EIMS *m/z* (% rel int.): 428 (M⁺, 84), 413 (23), 385 (28), 358 (20), 330 (65), 315 (100), 288 (51), 287 (44), 273 (32), 260 (25), 245 (22), 232 (28), 217 (32), 189 (27), 96 (26), 91 (31), 69 (76). ¹H and ¹³C NMR spectral data, see Table 3.

Acknowledgements

We are grateful to the Thailand Research Fund through the Royal Golden Jubilee Ph.D. Program for a scholarship to A. Hiranrat. The Center of Excellence for Innovation in Chemistry (PERCH-CIC), Commission on Higher Education, Ministry of Education, the Commission on Higher Education (CHE-RES-RG) and the Graduate School, Prince of Songkla University are gratefully acknowledged for the financial support. Finally, we also thank Assoc. Prof. Dr. Supayang Voravuthikulchai, Department of Microbiology, Faculty of Science, Prince of Songkla University, for providing the plant material.

References and notes

- Ruqiang, H.; Yonglu, C. *Abstracts of Papers*, 232nd ACS National Meeting, San Francisco, CA, Sept. 10–14, 2006; American Chemical Society: Washington, DC, 2006; AGFD-113.
- Dachriyanus; Salni; Sargent, M. V.; Skelton, B. W.; Soediro, I.; Sutisna, M.; White, A. H.; Yulinah, E. Aust. J. Chem. 2002, 55, 229.
- Magota, H.; Suzuki, M.; Uda, M.; Kyo, K.; Chin, G. Patent JP 04178324, 1992; Chem. Abstr. 1992, 117, 245608.
 Ministry P. Paters IP 2000100077, 2000. Chem. Abstr. 2000, 145
- Miyake, Y.; Nojima, J. Patent JP 2006199678, 2006; Chem. Abstr. 2006, 145, 173623.
- Hou, A. J.; Wu, Y. J.; Liu, Y. Z. Zhongcaoyao 1999, 30, 645; Chem. Abstr. 1999, 132, 234270.
- Dachriyanus; Fahmi, R.; Sargent, M. V.; Skelton, B. W.; White, A. H. Acta Crystallogr., E: Struct. Rep. Online 2004, E60, 086.
- Liu, Y. Z.; Hou, A. J.; Ji, C. R.; Wu, Y. J. Tianran Chanwu Yanjiu Yu Kaifa 1998, 10, 14; Chem. Abstr. 1998, 130, 136542.
- 8. Hui, W.-H.; Li, M.-M. Phytochemistry 1976, 15, 1741.
- 9. Terashima, S.; Shimizu, M.; Nakayama, H.; Ishikura, M.; Ueda, Y.; Imai, K.; Suzui, A.; Morita, N. *Chem. Pharm. Bull.* **1990**, *38*, 2733.
- 10. Crow, W. D.; Nicholls, W.; Sterns, M. Tetrahedron Lett. 1971, 18, 1353.
- D'Abrosca, B.; DellaGreca, M.; Fiorentino, A.; Monaco, P.; Oriano, P.; Temussi, F. Phytochemistry 2004, 65, 497.
- 12. Fukuyama, Y.; Minami, H.; Kuwayama, A. Phytochemistry **1998**, 49, 853.
- Shaheen, F.; Ahmad, M.; Khan, S. N.; Hussain, S. S.; Anjum, S.; Tashkhodjaev, B.; Turgunov, K.; Sultankhodzhaev, M. N.; Choudhary, M. I.; Atta-ur-Rahman. *Eur. J.* Org. Chem. **2006**, 2371.
- 14. Bloor, S. J. J. Nat. Prod. 1992, 55, 43.
- Appendino, G.; Bianchi, F.; Minassi, A.; Sterner, O.; Ballero, M.; Gibbons, S. J. Nat. Prod. 2002, 65, 334.