

## Friedolanostanes and Lanostanes from the Leaves of *Garcinia hombroniana*

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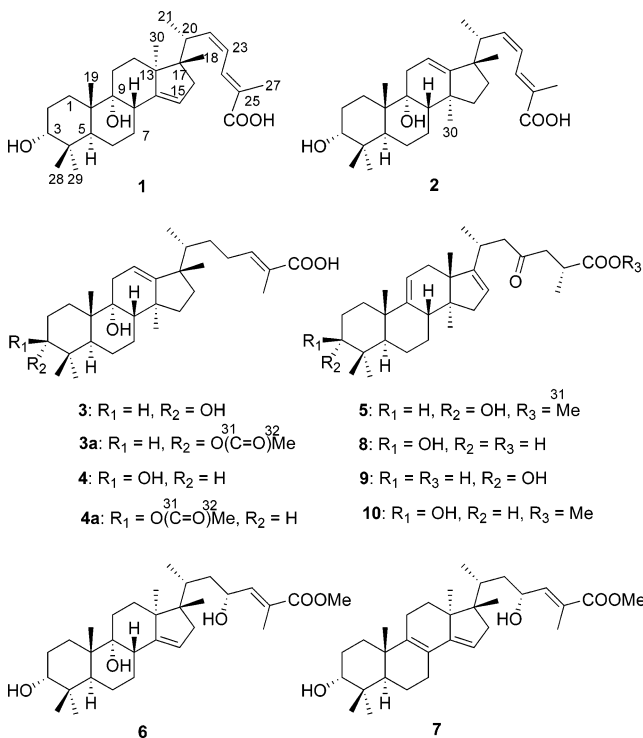
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Five new triterpenes, one 17,14-friedolanostane (garcihombronane F, **1**), three 17,13-friedolanostanes (garcihombronanes G–I, **2–4**), and one lanostane (garcihombronane J, **5**), were isolated from the leaves of *Garcinia hombroniana* together with nine known compounds including five triterpenes, two ionone-derived glycosides, and two flavonoid glucosides. Their structures were identified by analysis of spectroscopic data and comparison of the NMR data with those previously reported.

*Garcinia hombroniana* Pierre (Guttiferae), locally named “Wa”, is distributed in the southern part of Thailand. Plants in the genus *Garcinia* are well known to be rich in prenylated xanthenes. However, there have been three reports on the isolation of lanostanes and friedolanostanes from *G. hombroniana*<sup>1</sup> and *G. speciosa*.<sup>2,3</sup> In our ongoing search for new antibacterial substances active against methicillin-resistant *Staphylococcus aureus*, from *Garcinia* plants collected in the southern part of Thailand, a methanol extract of the leaves of *G. hombroniana* was investigated. Several lanostane- and friedolanostane-type triterpenes were isolated from the extract and examined for their antibacterial activity.

to yield five new triterpenes, garcihombronanes F–J (**1–5**), together with nine known compounds: five triterpenes [garcihombronanes B–E (**6–9**)<sup>1</sup> and methyl (25*R*)-3 $\beta$ -hydroxy-23-oxo-9,15-lanostadien-26-oate (**10**)<sup>2</sup>], two flavonoid glucosides (vitexin<sup>4</sup> and isovitexin<sup>5</sup>), and two ionone glycosides (blumenol C 9-*O*- $\beta$ -D-apiofuranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside<sup>6</sup> and vomifoliol 9-*O*- $\beta$ -D-apiofuranosyl-(1 $\rightarrow$ 6)- $\beta$ -D-glucopyranoside<sup>7</sup>). The structures of the new compounds were elucidated by analysis of 1D and 2D NMR spectroscopic data, while the known compounds were identified by comparison of their spectroscopic data, especially <sup>1</sup>H and <sup>13</sup>C NMR data, with those of known compounds. All <sup>13</sup>C NMR signals were assigned from DEPT, HMQC, and HMBC spectra. Compounds **3** and **4** were isolated and identified as their monoacetate derivatives (**3a** and **4a**).

Garcihombronane F (**1**), a white solid, had the molecular formula C<sub>30</sub>H<sub>46</sub>O<sub>4</sub> by HREIMS. The IR spectrum revealed the presence of a hydroxyl group (3436 cm<sup>-1</sup>) and a carbonyl group of an  $\alpha,\beta$ -unsaturated carboxylic acid (1681 cm<sup>-1</sup>). In the UV spectrum, a strong absorption band at 267 nm indicated that **1** possessed a conjugated carboxylic acid chromophore. The carbonyl functionality was further confirmed by a carbon signal at  $\delta$  173.1 in the <sup>13</sup>C NMR spectrum (Table 1). The <sup>1</sup>H NMR data (Table 1) were similar to those of **6**. HMBC cross-peaks between an olefinic proton ( $\delta$  5.34) and C-13 ( $\delta$  49.2), C-16 ( $\delta$  44.1), and C-17 ( $\delta$  53.7) established the position of a trisubstituted double bond in the tetracyclic system at C-14/C-15, the same position as that in **6**. The differences were observed in the <sup>1</sup>H NMR data of the side chain. Apart from the olefinic proton (H-15) in the tetracyclic structure, three olefinic protons [ $\delta$  7.66 (d, *J* = 12.0 Hz), 6.21 (t, *J* = 12.0 Hz), and 5.97 (t, *J* = 12.0 Hz)], vinylic methyl protons ( $\delta$  1.94, s), and secondary methyl protons ( $\delta$  0.93, d, *J* = 7.5 Hz) were detected. These data established the structure of the side chain as [–CH(Me)CH=CH–CH=C(Me)COOH]. The <sup>3</sup>*J* cross-peaks in the HMBC spectrum of H-22 ( $\delta$  5.97)/C-24 ( $\delta$  135.0), H-23 ( $\delta$  6.21)/C-20 ( $\delta$  36.9) and C-25 ( $\delta$  126.2), and H-24 ( $\delta$  7.66)/C-22 ( $\delta$  144.1), C-26 ( $\delta$  173.1), and C-27 ( $\delta$  12.1) supported the proposed side chain. Irradiation of H-24 did not affect Me-27 ( $\delta$  1.94), while irradiation of H-22 enhanced the signal of H-23. These observations indicated that the configurations of double bonds at C22/C23 and C24/C25 of the side chain were *Z* and *E*, respectively. Furthermore, HMBC cross-peaks of both Me-21 and H-22 with the same quaternary C-17 confirmed the attachment of the side chain at C-17. The location of all tertiary methyl groups as well as two hydroxyl groups was identical to



### Results and Discussion

The crude methanol extract from the leaves of *G. hombroniana* was separated by chromatographic methods

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**Table 1.** <sup>1</sup>H and <sup>13</sup>C NMR Data of Garcihombronanes **1**, **2**, **3a**, **4a**, and **5**

Position	<b>1</b>		<b>2</b>		<b>3a</b>		<b>4a</b>		<b>5</b>	
	$\delta_H$	$\delta_C$	$\delta_H$	$\delta_C$	$\delta_H$	$\delta_C$	$\delta_H$	$\delta_C$	$\delta_H$	$\delta_C$
1	a: 1.88 (m) b: 1.15 (m)	23.5	a: 1.98 (m) b: 1.06 (m)	23.6	a: 1.86 (m) b: 1.13 (m)	24.3	a: 1.72 (m) b: 1.60 (m)	23.6	a: 1.82 (m) b: 1.53 (m)	30.5
2	a: 2.00 (m) b: 1.90 (m)	25.0	a: 1.93 (m) b: 1.65 (m)	25.0	a: 1.84 (m) b: 1.65 (m)	22.7	a: 1.78 (m) b: 1.37 (m)	28.8	a: 2.01 (td, 14.0, 3.0) b: 1.70 (m)	25.6
3	3.38 (brs)	76.1	3.39 (brs)	76.2	4.63 (brs)	78.1	4.50 (dd, 11.5, 4.5)	80.1	3.44 (brs)	76.2
4		37.5		37.5		36.6		37.6		37.9
5	1.97 (m)	38.9	1.98 (m)	39.2	1.99 (m)	40.5	1.65 (m)	45.2	1.35 (dd, 12.0, 2.0)	46.7
6	a: 1.62 (m) b: 1.42 (m)	25.0	a: 1.57 (m) b: 1.33 (m)	21.1	a: 1.58 (m) b: 1.33 (m)	20.9	a: 1.65 (m) b: 1.37 (m)	21.0	a: 1.59 (m) b: 1.50 (m)	21.1
7	a: 1.55 (m) b: 1.36 (m)	20.6	a: 1.70 (m) b: 1.53 (m)	23.2	1.61 (m)	23.1	a: 1.65 (m) b: 1.53 (m)	23.0	a: 1.73 (m) b: 1.44 (m)	27.9
8	2.31 (m)	39.1	1.30 (m)	47.3	1.34 (m)	47.3	1.31 (m)	47.2	2.35 (m)	40.0
9		75.6		77.2		77.0		76.0		149.4
10		42.2		42.6		42.6		42.5		39.6
11	a: 1.54 (m) b: 1.83 (m)	29.5	a: 2.50 (dd, 19.5, 4.8) b: 1.83 (dd, 19.5, 2.7)	35.4	a: 2.50 (dd, 19.5, 5.0) b: 1.97 (m)	35.1	a: 2.50 (dd, 19.5, 5.5) b: 1.95 (dd, 19.5, 2.5)	35.3	5.32 (brd, 6.0)	114.2
12	a: 1.55 (m) b: 1.37 (m)	27.5	5.11 (dd, 4.8, 2.7)	116.6	5.18 (dd, 5.0, 2.5)	115.5	5.17 (dd, 5.5, 2.5)	115.5	a: 2.35 (m) b: 1.77 (m)	31.1
13		49.2		154.9		156.9		156.8		50.9
14		153.5		45.2		45.2		45.0		46.7
15	5.34 (brs)	119.9	a: 1.61 (m) b: 1.23 (m)	38.8	a: 1.58 (m) b: 1.22 (m)	38.7	a: 1.57 (m) b: 1.21 (m)	38.8	a: 2.07 (brd, 15.5) b: 1.83 (dd, 15.5, 3.5)	40.8
16	a: 2.37 (dd, 15.0, 3.5) b: 1.85 (m)	44.1	a: 1.93 (m) b: 1.34 (m)	34.2	a: 1.77 (m) b: 1.27 (m)	34.0	a: 1.78 (m) b: 1.29 (m)	34.1	5.22 (brs)	120.3
17		53.7		48.0		48.7		48.7		155.7
18	0.89 (s)	15.6	0.93 (s)	26.4	0.95 (s)	26.4	0.94 (s)	26.2	0.75 (s)	19.4
19	0.90 (s)	16.3	0.84 (s)	16.8	0.87 (s)	16.9	0.88 (s)	17.0	1.08 (s)	21.9
20	3.21 (dq, 12.0, 7.5)	36.9	2.82 (dq, 11.4, 6.0)	41.7	1.46 (m)	41.9	1.45 (m)	41.9	2.69 (m)	28.0
21	0.93 (d, 7.5)	17.7	1.00 (d, 6.0)	16.9	0.89 (d, 7.0)	15.4	0.89 (d, 8.0)	15.4	1.04 (d, 7.0)	21.1
22	5.97 (t, 12.0)	144.1	5.75 (t, 11.4)	144.6	a: 1.82 (m) b: 1.11 (m)	30.7	a: 1.81 (m) b: 1.10 (m)	30.7	a: 2.66 (dd, 19.0, 6.5) b: 2.46 (dd, 19.0, 6.5)	49.5
23	6.21 (t, 12.0)	121.9	6.31 (t, 11.4)	123.6	a: 2.30 (m) b: 2.05 (m)	27.6	a: 2.26 (m) b: 2.07 (m)	27.6		208.2
24	7.66 (d, 12.0)	135.0	7.50 (d, 11.4)	135.8	6.90 (qt, 7.5, 1.5)	145.7	6.90 (qt, 7.5, 1.5)	145.7	a: 2.87 (dd, 18.0, 8.0) b: 2.47 (m)	46.6
25		126.2		125.5		126.6		126.5	2.95 (quintet, 7.0)	34.5
26		173.1		172.0		172.3		172.3		176.3
27	1.94 (s)	12.1	1.93 (d, 1.2)	12.2	1.84 (s)	12.1	1.84 (s)	12.1	1.16 (d, 7.0)	17.1
28	0.84 (s)	22.0	0.84 (s)	22.2	0.91 (s)	21.8	0.90 (s)	28.1	0.89 (s)	22.5
29	0.96 (s)	28.4	0.97 (s)	28.5	0.88 (s)	28.0	0.87 (s)	16.4	0.97 (s)	28.4
30	1.10 (s)	18.7	1.10 (s)	19.2	1.02 (s)	19.7	1.00 (s)	19.8	0.82 (s)	19.9
31						170.9		171.0	3.68 (s)	51.8
32					2.06 (s)	21.4	2.04 (s)	21.3		

those of **6**, on the basis of similar HMBC correlations (see Supporting Information). Since H-3 ( $\delta$  3.38) appeared as a broad singlet, it was located at the  $\beta$ -equatorial position.<sup>1</sup> The remaining relative stereochemistry was identical to **6** on the basis of the identical NOEDIFF data (see Supporting Information). Thus, garcihombronane F (**1**) was identified as (2Z,24E)-3 $\alpha$ ,9 $\alpha$ -dihydroxy-17,14-friedolanostan-14,22,-24-trien-26-oic acid, a new 17,14-friedolanostane.

Garcihombronane G (**2**), a colorless gum, displayed the molecular formula C<sub>30</sub>H<sub>46</sub>O<sub>4</sub> by HREIMS of [M - H<sub>2</sub>O]<sup>+</sup>. The IR and UV spectra showed absorption bands similar to those of **1**. The carbonyl functionality of an unsaturated

acid was confirmed by a <sup>13</sup>C NMR signal at  $\delta$  172.0. The <sup>13</sup>C NMR spectrum (Table 1) together with data from DEPT experiments showed that the number and type of carbons were identical to those of **1**. Thus, **2** had a tetracyclic core structure with a 3 $\alpha$ -axial hydroxyl group and the same side chain as that of **1**. However, an olefinic proton at  $\delta$  5.11 (dd,  $J$  = 4.8 and 2.7 Hz) correlated with C-9 ( $\delta$  77.2) and C-14 ( $\delta$  45.2), suggesting that the trisubstituted double bond was located at C-12/C-13, a position different from that in **1**. In addition, the <sup>3</sup> $J$  correlations of Me-30 with C-8 ( $\delta$  47.3), C-13 ( $\delta$  154.9), and C-15 ( $\delta$  38.8) established the attachment of Me-30 at C-14, not C-13 as in **1**. The

locations of other tertiary methyl groups and a hydroxyl group of a tertiary alcohol were the same as those of **1**, on the basis of the HMBC correlations (see Supporting Information). The relative stereochemistry of Me-30 was deduced by NOE difference spectral data. Irradiation of  $\beta$ -axial H-8 did not enhance the signal intensity of Me-30, indicating their *trans* relationship. The remaining stereochemistry was found to be the same as in **1**, based on the NOEDIFF data (see Supporting Information). Garcihombrobronane G (**2**) was therefore assigned as (2*Z*,24*E*)-3 $\alpha$ ,9 $\alpha$ -dihydroxy-17,13-friedolanostan-12,22,24-trien-26-oic acid, the first 17,13-friedolanostane isolated from *G. hombroniana*.

Garcihombrobronane H (**3**), a colorless gum, was identified as its monoacetate derivative (**3a**). The monoacetate showed the molecular formula of C<sub>32</sub>H<sub>50</sub>O<sub>5</sub> by HREIMS of [M – H<sub>2</sub>O]<sup>+</sup>. The IR spectrum showed absorption bands for a hydroxyl group (3419 cm<sup>-1</sup>) and carbonyl groups of an  $\alpha,\beta$ -unsaturated carboxylic acid (1646 cm<sup>-1</sup>) and a saturated ester (1716 cm<sup>-1</sup>). In the UV spectrum, a strong absorption band at shorter wavelength than those in **1** and **2** indicated the presence of a less conjugated chromophore. The carbonyl functionalities were confirmed by carbon signals at  $\delta$  172.3 and 170.9 in the <sup>13</sup>C NMR spectrum (Table 1). The appearance of  $\beta$ -equatorial H-3 at much lower field ( $\delta$  4.63, brs) than was found in **1** and **2**, together with its HMBC correlation with the ester carbonyl carbon ( $\delta$  170.9), established attachment of the acetoxy group at C-3. The <sup>1</sup>H NMR spectrum exhibited only two olefinic protons, at  $\delta$  5.18 (dd, *J* = 5.0 and 2.5 Hz) and 6.90 (qt, *J* = 7.5 and 1.5 Hz), indicating one less double bond. These data together with the <sup>13</sup>C NMR and DEPT data revealed the presence of two trisubstituted double bonds. Signals of the low-field olefinic proton, a vinylic methyl group ( $\delta$  0.88, s), and a secondary methyl group ( $\delta$  0.89, d, *J* = 7.0 Hz) established the structure of the side chain to be [–CH(Me)–CH<sub>2</sub>CH<sub>2</sub>CH=C(Me)COOH]. The structure of the side chain was further confirmed by HMBC data (see Supporting Information). The configuration of the C24/C25 double bond of the side chain was identical to that of **2** since the enhancement of Me-27 was not observed by irradiation of H-24 ( $\delta$  6.90). The other olefinic proton (H-12) correlated with C-9 ( $\delta$  77.0), C-14 ( $\delta$  45.2), and C-17 ( $\delta$  48.7) in the HMBC spectrum, suggesting the other trisubstituted double bond to be at C-12/C-13, the same position as that in **2**. Thus, on the basis of studies of the 3-acetoxy derivative, garcihombrobronane H (**3**) was identified as shown.

Garcihombrobronane I (**4**) was also identified as its monoacetate derivative (**4a**), which showed the same molecular formula as that of **3a**. Their UV and IR data were similar, suggesting that they had the same chromophores and functional groups. The <sup>1</sup>H NMR spectrum (Table 1) was almost identical to that of **3a** except for the appearance of H-3 in **4a** as doublet of doublets ( $\delta$  4.50, *J* = 11.5 and 4.5 Hz), instead of a broad singlet. Thus, **4** differed from **3** only in the spatial arrangement of H-3 at an  $\alpha$ -axial position. This conclusion was confirmed by signal enhancement of both H-3 and H-5, upon irradiation of  $\alpha$ -equatorial Me-29. Therefore, **4** was a  $3\beta$  isomer of **3**.

Garcihombrobronane J (**5**) was obtained as a colorless gum with the molecular formula C<sub>31</sub>H<sub>48</sub>O<sub>4</sub> (HREIMS). The IR spectrum indicated a hydroxyl group (3476 cm<sup>-1</sup>), a ketone carbonyl (1716 cm<sup>-1</sup>), and an ester carbonyl (1734 cm<sup>-1</sup>). In the UV spectrum, a strong absorption band at 207 nm indicated that **5** possessed the same chromophore as **10**.<sup>2</sup> Furthermore, their <sup>1</sup>H NMR (Table 1) and NOE difference data were almost identical. The difference was the multi-

plicity of the oxymethine proton, H-3 ( $\delta$  3.44), which appeared in **5** as a broad singlet. These data suggested that H-3 was  $\beta$ -equatorial. This conclusion was confirmed by signal enhancement of Me-29, not H-3, upon irradiation of H-5 ( $\delta$  1.35, dd, *J* = 12.0 and 2.0 Hz). The stereochemistry at C-25 was assigned to be identical to that of compounds **8** and **9** on the basis of the multiplicity and coupling constant of H-25.<sup>2</sup> Therefore, **5** was the C-3 epimer of **10**.

The lanostanoid and friedolanostanoid triterpenes isolated (**1**–**10**) showed essentially no antibacterial activity against methicillin-resistant *Staphylococcus aureus* (MRSA), all having a minimum inhibitory concentration (MIC) of >128  $\mu$ g/mL, while the standard, vancomycin, had a MIC value of 2  $\mu$ g/mL.

## Experimental Section

**General Experimental Procedures.** Melting points were determined on an electrothermal melting point apparatus (Electrothermal 9100) and are reported without correction. Infrared spectra (IR) were obtained on a FTS165 FT-IR spectrometer and Perkin-Elmer spectrum GX FT-IR system. <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance spectra were recorded in deuterated chloroform solution on a FTNMR, Bruker Avance 300 MHz, or Varian UNITY INOVA 500 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. Ultraviolet (UV) spectra were measured with a UV-160A spectrophotometer (Shimadzu). Optical rotation was measured on an AUTOPOL II automatic polarimeter. Column chromatography was performed on silica gel (Merck) type 100 (70–230 mesh ASTM) using a gradient system of increasing polarity (MeOH–CHCl<sub>3</sub>), silica gel 60 RP-18 (40–63  $\mu$ m) (Merck) with a gradient system of decreasing polarity (MeOH–H<sub>2</sub>O), or Sephadex LH-20 with pure MeOH or as otherwise stated. Flash column chromatography was carried out on silica gel (Merck) type 60 (230–400 mesh ASTM). Thin-layer chromatography (TLC) and pre-coated TLC were performed on silica gel 60 F<sub>254</sub> or RP-18 F<sub>254s</sub> (Merck). Light petroleum had bp 40–60 °C. Acetylation was performed using a sample (20 mg) and acetic anhydride (0.5 mL) in the presence of pyridine (0.2 mL). The reaction mixture was stirred at room temperature overnight. Ice water was added, and the mixture was then extracted with ethyl acetate (3  $\times$  20 mL). The ethyl acetate layer was consecutively washed with 10% HCl (2  $\times$  20 mL), 10% NaHCO<sub>3</sub> (3  $\times$  20 mL), and H<sub>2</sub>O (2  $\times$  20 mL). The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered, and evaporated to dryness in vacuo to yield a crude product mixture.

**Plant Material.** Leaves of *G. hombroniana* were collected at Prince of Songkla University, Hat Yai, Songkhla, Thailand, in 2000. A voucher specimen is deposited in the Herbarium of the Department of Biology, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, Thailand.

**Isolation.** The leaves of *G. hombroniana* (7.25 kg), cut into small segments, were extracted with MeOH (25 L). After filtration, the filtrate was evaporated under reduced pressure to give a crude MeOH extract (100 g), which was subsequently separated into two fractions by dissolving in light petroleum. The light petroleum-soluble fraction (16.2 g) was fractionated by column chromatography (CC) to afford eight fractions (A1–A8). Fraction A4 (2.1 g) was further purified by CC to yield three subfractions. Subfraction 2 (40 mg) was separated by CC, eluting with a gradient system of EtOAc–light petroleum, to afford **5** (2 mg) and **10**<sup>2</sup> (2 mg). Fraction A6 (2 g), upon CC, yielded four subfractions. Subfraction 2 (818 mg) was further subjected to CC to yield four subfractions. The second fraction (158 mg) was separated by TLC, using 10% EtOAc–CH<sub>2</sub>Cl<sub>2</sub>, to afford **8**<sup>1</sup> (2 mg), while the third subfraction (116 mg) was further purified by CC, eluting with a gradient system of acetone–CH<sub>2</sub>Cl<sub>2</sub> (10% to 80% acetone–CH<sub>2</sub>Cl<sub>2</sub>), to yield **6**<sup>1</sup> (8 mg) and **7**<sup>1</sup> (10 mg). Subfraction 3 (736 mg) was fractionated by CC to yield three subfractions. The third fraction (67 mg) was separated by CC to yield five subfractions. The second

subfraction was subjected to acetylation, and subsequent purification of the mixture of acetates by TLC, using 2% EtOAc-CH<sub>2</sub>Cl<sub>2</sub>, afforded **3a** (5 mg) and **4a** (4 mg). Fraction A8 (860 mg), upon CC, yielded **1** (52 mg). The light petroleum-insoluble fraction (80 g) was fractionated by flash CC, eluting with gradient systems of hexane-CHCl<sub>3</sub> and CHCl<sub>3</sub>-MeOH, to yield nine fractions (B1-B9). Fraction B4 (20 g), upon CC, yielded five subfractions. Subfraction 2 (73 mg) was subjected to flash CC, eluting with a gradient system of MeOH-EtOAc (50% MeOH-EtOAc to pure MeOH), to afford **9**<sup>1</sup> (4 mg). Subfraction 4 (74 mg) was separated by CC to afford **2** (5 mg). Vitexin<sup>4</sup> (5 mg) was obtained from the MeOH-insoluble fraction of fraction B8. The soluble fraction was then subjected to Sephadex LH20 to yield four subfractions. Subfraction 2 (3 g) was further purified by reversed-phase CC to yield four subfractions. The second (62 mg) and the third (47 mg) fractions were subjected to acetylation, and subsequent separation by CC, eluting with a gradient system of EtOAc-light petroleum (50% EtOAc-light petroleum to pure EtOAc), afforded the acetate derivatives of blumenol C 9-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside<sup>6</sup> (24 mg) and vomifoliol 9-*O*-β-D-apiofuranosyl-(1→6)-β-D-glucopyranoside<sup>7</sup> (17 mg), respectively. Subfraction 3 (582 mg), upon flash CC, yielded three subfractions. The second fraction was further subjected to Sephadex LH20 to afford isovitexin<sup>5</sup> (11 mg).

**Garcihombrone F (1)**: white solid, mp 154–157 °C;  $[\alpha]_D^{27} -154^\circ$  (*c* 0.026, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 267 (4.56); IR (neat)  $\nu_{\max}$  3436, 2964, 2932, 1681 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz), Table 1; <sup>13</sup>C NMR (125 MHz), Table 1; EIMS *m/z* 470 [M]<sup>+</sup> (2), 452 (52), 434 (17), 313 (74), 295 (80), 159 (100); HREIMS *m/z* 470.3350 (calcd for C<sub>30</sub>H<sub>46</sub>O<sub>4</sub>, 470.3396).

**Garcihombrone G (2)**: colorless gum;  $[\alpha]_D^{27} +125^\circ$  (*c* 0.024, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 268 (4.12); IR  $\nu_{\max}$  (neat) 3409, 2926, 1671 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz), Table 1; <sup>13</sup>C NMR (75 MHz), Table 1; EIMS *m/z* 452 [M - H<sub>2</sub>O]<sup>+</sup> (1), 149 (92), 83 (100); HREIMS *m/z* 452.3250 [M - H<sub>2</sub>O]<sup>+</sup> (calcd for C<sub>30</sub>H<sub>44</sub>O<sub>3</sub>, 452.3290).

**Garcihombrone H monoacetate (3a)**: colorless gum;  $[\alpha]_D^{27} -77^\circ$  (*c* 0.013, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 216 (3.64); IR  $\nu_{\max}$  (neat) 3419, 2932, 1716, 1646 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz), Table 1; <sup>13</sup>C NMR (125 MHz), Table 1; EIMS *m/z* 496

[M - H<sub>2</sub>O]<sup>+</sup> (2), 387 (35), 121 (100); HREIMS *m/z* 496.3529 [M - H<sub>2</sub>O]<sup>+</sup> (calcd for C<sub>32</sub>H<sub>48</sub>O<sub>4</sub> 496.3553).

**Garcihombrone I monoacetate (4a)**: colorless gum;  $[\alpha]_D^{27} -100^\circ$  (*c* 0.010, MeOH); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 216 (3.53); IR  $\nu_{\max}$  (neat) 3445, 2930, 1717, 1643 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz), Table 1; <sup>13</sup>C NMR (125 MHz), Table 1; EIMS *m/z* 496 [M - H<sub>2</sub>O]<sup>+</sup> (2), 387 (45), 313 (7), 121 (100); HREIMS *m/z* 496.3528 [M - H<sub>2</sub>O]<sup>+</sup> (calcd for C<sub>32</sub>H<sub>48</sub>O<sub>4</sub> 496.3553).

**Garcihombrone J (5)**: colorless gum;  $[\alpha]_D^{27} +95^\circ$  (*c* 0.021, CHCl<sub>3</sub>); UV (MeOH)  $\lambda_{\max}$  (log  $\epsilon$ ) 207 (3.45); IR  $\nu_{\max}$  (neat) 3476, 2929, 1734, 1716 cm<sup>-1</sup>; <sup>1</sup>H NMR (500 MHz), Table 1; <sup>13</sup>C NMR (125 MHz), Table 1; EIMS *m/z* 484 [M]<sup>+</sup> (38), 295 (77), 129 (100); HREIMS *m/z* 484.3560 (calcd for C<sub>31</sub>H<sub>48</sub>O<sub>4</sub> 484.3553).

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**Supporting Information Available:** Tables of selected HMBC correlations and NOEDIFF data of **1**–**5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## References and Notes

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