Terpenoids and a Diarylheptanoid from *Zingiber ottensii*

Kayo Akiyama,[†] Hiroe Kikuzaki,*[,†] Takako Aoki,[†] Akiko Okuda,[†] Nordin H. Lajis,[‡] and Nobuji Nakatani[§]

Graduate School of Human Life Science, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi, Osaka, Japan, Laboratory of Natural Products, Institute of Bioscience, University Putra Malaysia, 43400 Serdang, Selangor, Malaysia, and University of the Air, 2-11, Wakaba, Mihama, Chiba, Japan

Four new terpenoids and a diarylheptanoid were isolated together with 16 known compounds from rhizomes of *Zingiber ottensii*. The structures of the new compounds were determined to be 1,10,10-trimethylbicyclo[7,4,0]tridecane-3,6-dione (**1**), (*E*)-14-hydroxy-15-norlabda-8(17),12-dien-16-al (**2**), (*E*)-labda-8(17),12,14-trien-15(16)-olide (**3**), (*E*)-14,-15,16-trinorlabda-8(17),11-dien-13-oic acid (**4**), and *rel*-(3*R*,5*S*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(3,4-dihydroxyphenyl)heptane (**5**) by spectroscopic evidence.

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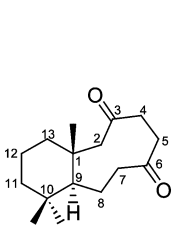
Rhizomes of many plants belonging to the genus *Zingiber* (Zingiberaceae) are used as spices or traditional folk medicines in many parts of the world. In the course of investigation of phytochemical constituents of the Zingiberaceae plants of Malaysia,[1a,b] we focused on *Zingiber ottensii* Val. (Zingiberaceae), which is cultivated in Malaysia and used in traditional medicine for its sedative effect.[2] Constituents isolated previously from rhizomes of *Z. ottensii* were reported to be terpenoids such as humulene, zerumbone, zerumbone epoxide, and (*E*)-labda-8(17),12-diene-15,-16-dial.[3] In this paper, we describe the structural elucidation of four new terpenoids (**1**−**4**) and a diarylheptanoid (**5**) isolated from the rhizomes of this plant.



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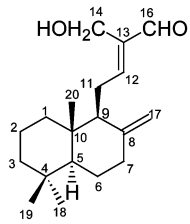

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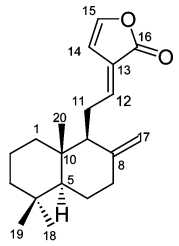

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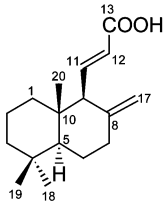

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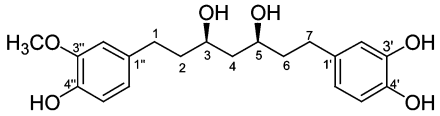

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A freeze-dried rhizome of *Z. ottensii* was extracted with CH_2Cl_2 at room temperature. The CH_2Cl_2 extract was subjected to successive column chromatography using Sephadex LH-20, silica gel, and Chromatorex ODS to give four new terpenoids (**1**−**4**) and 16 known compounds. Among them, zerumbone[4,5] and (*E*)-8(17),12-labdadiene-15,16-dial,[6] which are known as characteristic terpenoids from Zingiberaceae species,[7] were the major compounds isolated from *Z. ottensii*. Labdane-type diterpenes, such as zerumin A, coronarin B, and coronarin D, were identified by comparison of the spectral data with those in the literature.[6,8,9] Other known compounds including zerumbone epoxide,[5] eudesmane-4α,11-diol,[10,11] 3,4′-*O*-dimethyl[12] and 3,7,4′-*O*-trimethyl kaempferols,[13] eicosyl ferulate,[14] 5-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(4-hydroxyphenyl)heptan-3-one,[15] and a mixture of kaempferol 3-*O*-(2,4-*O*-diacetyl)-α-L-rhamnopyranoside and kaempferol 3-*O*-(3,4-*O*-diacetyl)-α-L-rhamnopyranoside[5,12] were also isolated.

The residue, after extraction with CH_2Cl_2, was extracted with 70% aqueous acetone, and the aqueous extract was partitioned with EtOAc and H_2O. The EtOAc-soluble fraction was subjected to column chromatography to isolate kaempferol 3-*O*-α-L-rhamnopyranoside, kaempferol 3-*O*-(2-*O*-acetyl)-α-L-rhamnopyranoside, and kaempferol 3-*O*-(3-*O*-acetyl)-α-L-rhamnopyranoside,[16] in addition to compound **5**.

Compound **1** was obtained as a colorless oil. The EIMS gave an $[M]^+$ peak at *m*/*z* 250. The molecular formula was determined to be $C_{16}H_{26}O_2$ by HREIMS. The ^{13}C NMR spectrum showed 16 signals, two of which appeared at δ 212.0 and 213.0, indicating the presence of two carbonyl carbons. An IR absorption band at 1710 cm^{-1} further supported the presence of these carbonyls. The ^1H NMR spectrum showed singlets at δ 0.87, 0.88, and 1.01 corresponding to three methyl groups, and the other higher field signals [δ 1.80 (1H, br ddd, J = 13, 13, 3 Hz), δ 1.32 (1H, m), δ 1.40 (1H, m), δ 1.57 (1H, m), δ 1.16 (1H, br ddd, J = 13, 13, 3 Hz), δ 1.34 (1H, m), δ 0.95 (1H, dd, J = 5, 3 Hz)] were similar to those of the respective H-1, H-2, H-3, and H-5 in (*E*)-8(17),12-labdadiene-15,16-dial.[6] The two doublets at δ 1.96 and 2.49 coupled with each other with a coupling constant of 14 Hz, both of which showed correlations with a carbon at δ 54.3 in the HMQC spectrum, and with four carbons at δ 21.3 (C-Me1), 41.1 (C-1), 51.5 (C-9), and 212.0 (C-3) in the HMBC spectrum. In addition, the protons of Me-1 correlated with C-1, C-2, C-9, and C-13. The $^1H-^1H$ COSY spectrum indicated that two pairs of geminal protons [δ 2.44 (m) and δ 2.82 (ddd, J = 13, 13, 4 Hz), δ 2.41 (m) and δ 3.05 (ddd, J = 13, 13, 3 Hz)] were vicinal. These protons were correlated to the carbonyl carbon at δ 212.0 and/or δ 213.0 in the HMBC spectrum. Similarly, the geminal protons of C-7 at δ 2.39 (ddd, J = 13, 13, 4 Hz) and δ 2.66 (ddd, J = 13, 6, 4 Hz) were correlated to the carbon at δ 213.0. These results suggested that compound **1** had a bicycle [7,4,0]tridecane skeleton.

There was no correlation between the methyl protons at Me-1 (δ 1.01) and H-9 (δ 0.95) in the NOESY spectrum of compound **1**, which confirmed the relationship between Me-1 and H-9 to be *trans* (see Supporting Information). Thus, the relative structure of compound **1** was defined as *rel*-1*R*,9*S*-1,10,10-trimethylbicyclo-[7,4,0]tridecane-3,6-dione. This is the first report of a compound having this skeleton as a natural product.

Compound **2** was obtained as white, amorphous solid, which showed a molecular weight of 290 by EIMS measurement and a

* To whom correspondence should be addressed. Tel: +81-6-6605-2812. Fax: +81-6-6605-3086. E-mail: kikuzaki@life.osaka-cu.ac.jp.
[†] Osaka City University.
[‡] University Putra Malaysia.
[§] University of the Air.

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Table 1. ^{1}H and ^{13}C NMR Data (500 Mz, $CDCl_3$) of Diterpenoids Isolated from *Z. ottensii*[a]

	2			**3**			**4**		
	δ_H		δ_C	δ_H		δ_C	δ_H		δ_C
1α	1.10	br ddd (13, 13, 4)	39.3	1.18	br ddd (13, 13, 4)	39.0	1.03	br ddd (13, 13, 4)	40.8
1*β*	1.74	m		1.88	m		1.35−1.45[b]	m	
2α	1.53	m	19.4	1.53	m	19.4	1.35−1.45[b]	m	19.0
2*β*	1.60	ddddd (13, 13, 13, 3, 3)		1.60	ddddd (13, 13, 13, 3, 3)		1.53	ddddd (13, 13, 13, 3, 3)	
3α	1.20	br ddd (13, 13, 4)	42.0	1.20	br ddd (13, 13, 4)	42.0	1.19	br ddd (13, 13, 4)	42.1
3*β*	1.43	dddd (13, 3, 3, 1.5)		1.41	dddd (13, 3, 3, 2)		1.35−1.45[b]	m	
4			33.6			33.6			33.5[c]
5	1.15	dd (13, 3)	55.4	1.17	dd (13, 3)	55.5	1.09	dd (13, 3)	54.4
6α	1.76	dddd (13, 5, 3, 3)	24.2	1.76	dddd (13, 5, 3, 3)	24.4	1.72	dddd (13, 5, 3, 3)	23.2
6*β*	1.36	dddd (13, 13, 13, 4)		1.36	dddd (13, 13, 13, 4)		1.35−1.45[b]	m	
7α	2.03	br ddd (13, 13, 5)	37.9	1.99	br ddd (13, 13, 5)	38.1	2.09	br ddd (13, 13, 5)	35.6
7*β*	2.42	ddd (13, 4, 2)		2.38	ddd (13, 4, 2)		2.45	ddd (13, 4, 2)	
8			148.0			147.7			148.3
9	1.91	br d (11)	56.7	2.01	br d (12)	53.9	2.51	br d (11)	60.6
10			39.7			40.0			39.3
11	2.47	ddd (17, 11, 7)	24.1	2.45	ddd (16, 12, 1)	19.5	7.15	dd (16, 11)	150.8
	2.64	ddd (17, 6, 3)		2.69	ddd (16, 2, 1)				
12	6.58	dd (7, 6)	158.6	7.52	ddd (1, 1, 1)	153.0	5.83	d (16)	122.7
13			140.9			129.8			169.6
14	4.40	br s	56.2	7.67	dd (6, 1)	154.6			
15				6.31	d (6)	116.4			
16	9.37	s	195.9			178.8			
17	4.42	br d (1)	108.0	4.46	br d (1)	107.8	4.43	br d (1)	108.8
	4.86	br d (1)		4.82	br d (1)		4.79	br d (1)	
18	0.89	s	33.6	0.88	s	33.6	0.90	s	33.6[c]
19	0.83	s	21.7	0.82	s	21.7	0.84	s	21.9
20	0.75	s	14.4	0.78	s	14.4	0.89	s	15.0
OH	2.54	br s							

[a] Chemical shifts are shown in δ values (ppm) relative to TMS peak. The *J* values (Hz) are in parentheses. [b] Overlapped signal. [c] Assignment are interchangeable in each column.

molecular formula of $C_{19}H_{30}O_2$ by HREIMS measurement. The ^{13}C NMR spectrum gave 19 signals, including one carbonyl carbon at δ 195.9. This carbon and a singlet signal at δ 9.37 in the ^{1}H NMR spectrum indicated the presence of an aldehyde group. IR absorption indicating an α,*β*-unsaturated carbonyl group was observed at 1685 cm^{-1}, as well as that for hydroxyl at 3430 cm^{-1} and those for an *exo*-methylene group at 3100, 1639, and 889 cm^{-1}. There were four olefinic carbons as indicated by the signals at δ 108.0, 140.9, 148.0, and 158.6 in the ^{13}C NMR spectrum. The ^{1}H NMR spectrum showed the presence of three methyl groups (δ 0.75, 0.83, and 0.89) and an *exo*-methylene (δ 4.42 and 4.86), which are characteristic of a labdane-type diterpenoid. The pattern of the ^{1}H NMR signals in the higher field region was similar to that of (*E*)-8(17),12-labdadiene-15,16-dial[6] (Table 1). In the ^{1}H−^{1}H COSY spectrum, the signal at δ 6.58 (1H, dd, J = 7, 6 Hz), which was deshielded due to the carbonyl group, was coupled to the signal at δ 2.47(1H, ddd, J = 17, 11, 7 Hz) and 2.64(1H, ddd, J = 17, 6, 3 Hz). The broad singlet of oxymethylene protons at δ 4.40 (2H) had HMBC correlations with the olefinic (δ 140.9 and 158.6) and the aldehydic (δ 195.0) carbons. These data indicated that the side chain attached at C-9 was 2-hydroxymethylbut-2-enal. The geometry of the olefin in this side chain was confirmed to be *E* on the basis of NOESY correlations between H-12 (δ 6.58) and the aldehydic proton (δ 9.37), as well as between H-11(δ 2.64) and H-14 (δ 4.40), in addition to the downfield shift of H-12.

The relative stereochemistry of compound **2** was determined on the basis of NOESY experiments. The NOESY correlations of H-20 with H-1*β* and H-6*β*, as well as of H-5 with H-7α, suggested that Me-20 and H-5 were in a *trans* orientation. Furthermore, the enal side chain was determined to be in *β*-orientation based on the NOESY correlation between H-9 and H-5. These results supported the structure of compound **2** as (*E*)-14-hydroxy-15-norlabda-8(17),12-dien-16-al, a norditerpenoid lacking C-15 of labdane-type diterpenes.

Compound **3** was obtained as a colorless oil and gave an $[M]^+$ peak at *m*/*z* 300 in the EIMS spectrum. The base ion peak at *m*/*z* 137 was characteristic of a labdane-type diterpene.[17] The molecular formula was determined to be $C_{20}H_{28}O_2$ by HREIMS. The ^{13}C NMR showed the presence of 20 carbons, with one of them being a carbonyl and six being olefinic. The ^{1}H NMR spectrum showed the presence of a bicyclic skeleton with three methyl groups and an *exo*-methylene, resembling that of (*E*)-8(17),12-labdadiene-15,16-dial.[6] In the IR spectrum, absorptions of *exo*-methylene (3050, 1644, 890 cm^{-1}) and lactone (1720 cm^{-1}) moieties were observed. The olefinic proton at δ 7.52 (1H, ddd, J = 1, 1, 1 Hz) was coupled with methylene protons at δ 2.45 and 2.69 (H-11). The other olefinic protons (δ 6.31 and 7.67) were mutually coupled with a coupling constant of 6 Hz, suggesting that they are *cis* to each other. Furthermore, the proton at δ 7.67 (H-14) showed long-range coupling with the proton at δ 7.52 (H-12). This finding and the HMBC correlations indicated the presence of conjugated double bonds. In the HMBC spectrum, the proton at δ 7.67 (H-14) correlated with carbons at δ 116.4 (C-15) and 178.8 (C-16), suggesting that compound **3** contained a lactone ring. The geometry between C-12 and C-13 was *E* configuration, as indicated by a downfield shift observed for H-12 and the absence of a NOESY correlation between H-12 and H-14. As in the case of compound **2**, the stereochemistry between Me-20 and H-5 for compound **3** was determined to be *trans* from the NOESY experiment. The orientation of C-11 was determined to be *β* on the basis of the NOESY correlations between H-11 (δ 2.45 and 2.69) and Me-20, as well as between H-5 (δ 1.17) and H-9 (δ 2.01). Thus, compound **3** was determined to be (*E*)-labda-8(17),12,14-trien-15(16)-olide. This compound was similar to coronarin D and isocoronarin D[18] isolated from *Hedychium coronarium* (Zingiberaceae).[9] Several labdane diterpenes possessing a *γ*-lactone ring like that in **3** have been isolated from plants of the Zingiberaceae.[19]

Compound **4** gave an $[M]^+$ peak at *m*/*z* 262 and had 17 carbons as determined by ^{13}C NMR measurement. The molecular formula was established as $C_{17}H_{26}O_2$, which was supported by HREIMS. The ^{1}H NMR spectrum indicated the presence of a bicyclic skeleton with three methyl groups and an *exo*-methylene, which suggested

Table 2. DPPH Radical Scavenging Activity of Compound **5** and Related Compounds[a]

	IC_{50} (μM)
compound **5**	24.0
(3*S*,5*S*)-1,7-di(4-hydroxy-3-methoxyphenyl)-3,5-heptanediol	20.1
(3*R*,5*S*)-1,7-di(4-hydroxy-3-methoxyphenyl)-3,5-heptanediol	20.6
(3*S*,5*S*)-1-(4-hydroxy-3,5-dimethoxyphenyl)-7-(4-hydroxy-3-methoxy)-3,5-heptanediol	16.4
L-ascorbic acid	35.6
α-tocopherol	37.5

[a] The concentration of DPPH radical was 100 μM in ethanol. The absorbance of the mixture at 520 nm against a blank of ethanol without DPPH was measured by a multilabel counter after 30 min.

that compound **4** was a labdane-type trinorditerpene. The carbon signal at δ 169.6 was assigned to a carboxyl group, and absorption bands at 1697 cm^{-1} and at 3600−2400 cm^{-1} observed in the IR spectrum supported its presence. The stereochemistry of the bicyclic skeleton was determined to be the same as that of (*E*)-8(17),12-labdadiene-15,16-dial,[6] compound **2**, or **3**. Two olefinic protons at δ 7.15 and 5.83 were mutually coupled with a coupling constant of 16 Hz, indicating that the geometry of the double bond was in *trans* configuration. The proton signal at δ 7.15 was assigned to H-11 because of its coupling with H-9. HMBC correlation observed between H-12 (δ 5.83) and a carboxyl carbon (δ 169.6) suggested that the carboxyl group was attached to C-12. These results supported the structure of compound **4** as (*E*)-14,15,16-trinorlabda-8(17),11-dien-13-oic acid. Other instances of nor-type labdanediterpenes isolated from Zingiberaceae include (*E*)-15,16-bisnorlabda-8(17)-dien-13-one isolated from *Alpinia speciosa*[20] and *A. formosana*[21] and 14,15,16-trinorlabda-8(17),11-(*E*)-dien-13-al isolated from *Hedychium coronarium*.[22]

Compound **5** was isolated from the EtOAc-soluble fraction. Peaks at *m*/*z* 362 ($[M]^+$) and 344 ($[M - H_2O]^+$) were detected by EIMS, and the molecular formula ($C_{20}H_{26}O_6$) was established by HREIMS measurement. The ^1H NMR spectrum showed the presence of two 1,3,4-trisubstituted phenyl moieties (δ 6.52, 6.69, 6.70; and 6.64, 6.71, 6.81). The 3H singlet at δ 3.81 was assigned to a methoxyl group, which showed an HMBC correlation with C-3′ (δ 148.1). The signals at δ 7.29 (1H, br s) and 7.66 (2H, br s) indicated that **5** possessed three phenolic OH groups. Therefore, compound **5** contained both a 3,4-dihydroxyphenyl and a 4-hydroxy-3-methoxyphenyl group. The presence of two hydroxymethyne groups was revealed by the signals at δ 3.80 (2H, m), 4.22 (1H, d, J = 3 Hz, −O*H*), and 4.24 (1H, d, J = 3 Hz, −O*H*) in the ^1H NMR spectrum and the carbon signals at δ 71.1 and 71.7, both of which correlated with the proton signal at δ 3.80 in the HMQC experiment. The signals of five methylenes were assigned by $^1H-^1H$ COSY, HMQC, and HMBC measurements. Thus, compound **5** was determined to be 3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(3,4-dihydroxyphenyl)heptane.

The *rel*-(3*R*,5*S*)configuration of **5** was suggested by ^{13}C NMR data. In fact, the chemical shifts of C-3, 5 (δ 71.7, 71.1) and C-4 (δ 44.3) were different from those of the aglycone of (3*R*,5*R*)-3,5-dihydroxy-1-(4-hydroxy-3-methoxyphenyl)-7-(3,4-dihydroxyphenyl)-heptane 3-*O*-β-D-glucopyranoside (δ 68.7 and 45.6).[23] Furthermore, the specific rotation ($[\alpha]_D^{24}$ −1.3) of compound **5** was close to zero, suggesting a symmetrical structure for **5**. Unfortunately there was not enough material to synthesize the 1,3-dibenzoate for application of the CD exciton chirality method.

We evaluated the DPPH radical scavenging activity of compound **5** together with other diarylheptanoids isolated from *Z. officinale* (Table 2). Compound **5** had greater scavenging activity than that of L-ascorbic acid or α-tocopherol, but showed slightly lower activity than the other diarylheptanoids.

Experimental Section

General Experimental Procedures. Specific rotations were recorded on a Jasco P1030 polarimeter (Tokyo, Japan). EI and HREIMS were measured at 70 eV on a Hitachi M 2000 mass spectrometer (Hitachi Ltd., Tokyo, Japan). IR spectra were measured on a JASCO FT/IR685V. ^1H, ^{13}C, and 2D NMR spectra were obtained on a Varian Unity 500 spectrometer (500 Mz, Varian Inc., Palo Alto, CA) using TMS as an internal standard. Si gel 60 (70−230 mesh, Merk), Sephadex LH-20 (Pharmacia), and Chromatorex ODS DM1020T (100−200 mesh, Fuji Silysia Chemical) were used for column chromatography. Precoated Si gel 60 F_{254} plates (Merck) and ODS plates (Merck) were used for TLC. HPLC analysis was carried out with a pump (Hitachi) connected to a UV detector (Jasco) and an integrator (Hitachi) operating at 280 or 210 nm. The column for HPLC was a Mightysil RH-18 (5 μm, 4.6 × 250 mm). The mobile phase was the solvent of constant polarity (CH_3CN-H_2O or CH_3OH-H_2O).

Plant Material. Rhizomes of *Zingiber ottensii* were harvested from the Germplasm Unit of University Putra Malaysia in October 1999. A voucher specimen (No. ZO-16/44) has been deposited at the herbarium of the Biology Department, University Putra Malaysia, Serdang, Malaysia.

Extraction and Isolation. Freeze-dried rhizomes (400 g) of *Z. ottensii* were extracted with CH_2Cl_2 at room temperature. After filtration and evaporation, the extract (28.2 g) was subjected to silica gel column chromatography (CC) using hexane−acetone to yield fractions A−G. Every fraction was analyzed by HPLC using CH_3OH-H_2O (82:18) as eluant. Fraction B was subjected to silica gel CC (hexane−acetone, 9:1) to give fractions B1−B15. Among these fractions, fraction B6 was purified by silica gel CC (hexane−acetone) to give zerumbone (96 mg), and fraction B8 was separated in a similar way to give (*E*)-8(17),12-labdadiene-15,16-dial (70 mg). Fraction B9 was rechromatographed using Sephadex LH-20 (IPA), silica gel (benzene−acetone, 95:5), and ODS gel (CH_3OH-H_2O, 6:4) to give zerumbone epoxide (2 mg), compound **1** (4 mg), compound **2** (8 mg), compound **3** (3 mg), and 5-hydroxy-3,7,4′-trimethoxyflavone (4 mg). From fraction B10, coronarin B (9 mg) was obtained by CC using ODS gel (CH_3OH-H_2O, 6:4). Coronarin D (19 mg) was obtained from rechromatography of fraction C using Sephadex LH-20 (IPA) and silica gel (benzene−acetone, 95:5). Fraction D was separated by Sephadex LH-20 (IPA) followed by silica gel (benzene−acetone) CC to yield eicosyl ferulate (5 mg), zerumin A (13 mg), compound **4** (1 mg), eudesmane-4α,11-diol (45 mg), and 5,7-dihydroxy-3,4′-dimethoxyflavone (8 mg). Fraction E was subjected to ODS (CH_3CN-H_2O, 7:3) and Sephadex LH-20 (IPA) column chromatographies to give 5-hydroxy-1-(4-hydroxymethoxyphenyl)-7-(4-hydroxyphenyl)heptan-3-one (6.5 mg) and a mixture of kaempferol 3-*O*-(2,4-*O*-diacetyl)-α-L-rhamnopyranoside and kaempferol 3-*O*-(3,4-*O*-diacetyl)-α-L-rhamnopyranoside (6.5 mg).

The residue after extraction with CH_2Cl_2 was further extracted with 70% aqueous acetone. After filtration, acetone was evaporated under reduced pressure, and the aqueous extract was obtained. The extract was partitioned between EtOAc and H_2O to give the EtOAc-soluble (6.8 g) and H_2O-soluble fractions (23.0 g). The EtOAc-soluble fraction was subjected to Sephadex LH-20 CC using IPA to give eight fractions. Fraction 4 was rechromatographed on ODS gel (CH_3CN-H_2O, 3:7) followed by silica gel ($CH_2Cl_2-CH_3OH$, 9:1) to give compound **5** (2.9 mg), kaempferol 3-*O*-α-L-rhamnopyranoside (9.0 mg), kaempferol 3-*O*-(2-*O*-acetyl)-α-L-rhamnopyranoside (3.6 mg), and kaempferol 3-*O*-(3-*O*-acetyl)-α-L-rhamnopyranoside (3.9 mg).

Compound 1: colorless oil; $[\alpha]_D^{25}$ −5.6 (*c* 0.16, $CHCl_3$); IR (film) ν_{max} 2925, 1710, 1460 cm^{-1}; ^1H NMR ($CDCl_3$, 500 MHz) δ 0.87 (3H, s, Me-10α), 0.88 (3H, s, Me-10β), 0.95 (1H, dd, J = 5, 3 Hz, H-9), 1.01 (3H, s, Me-1), 1.16 (1H, br ddd, J = 13, 13, 3 Hz, H-11α), 1.32 (1H, m, H-13β), 1.34 (1H, m, H-11β), 1.40 (1H, m, H-12α), 1.57 (1H, m, H-12β), 1.75 (2H, m, H-8), 1.80 (1H, br ddd, J = 13, 13, 3 Hz, H-13α), 1.96 (1H, d, J = 14 Hz, H-2α), 2.39 (1H, ddd, J = 13, 13, 4

Hz, H-7α), 2.41 (1H, m, H-5*β*), 2.44 (1H, m, H-4α), 2.49 (1H, d, *J* = 14 Hz, H-2*β*), 2.66 (1H, ddd, *J* = 13, 6, 4 Hz, H-7*β*), 2.82 (1H, ddd, *J* = 13, 13, 4 Hz, H-4*β*), 3.05 (1H, ddd, *J* = 13, 13, 3 Hz, H-5α); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ* 18.4 (C-12), 21.3 (Me-1), 21.7 (Me-10*β*), 21.9 (C-8), 33.4 (Me-10α), 35.5 (C-10), 36.4 (C-5), 39.9 (C-13), 41.1 (C-1), 41.6 (C-11), 43.3 (C-4), 47.5 (C-7), 51.5 (C-9), 54.3 (C-2), 212.0 (C-3), 213.0 (C-6); EIMS *m*/*z* 250 $[M]^+$ (5), 232 (6), 217 (14), 136 (58), 121 (36), 42 (100); HREIMS *m*/*z* 250.1936 (calcd for $C_{16}H_{26}O_2$, 250.1933).

Compound 2: white, amorphous solid; $[\alpha]^{25}_D$ +15.5 (*c* 0.15, $CHCl_3$); IR (film) ν_{max} 3430, 3100, 2929, 1685, 1639, 1460, 1023, 889 cm^{-1}; ^{1}H, ^{13}C NMR, see Table 1; EIMS *m*/*z* 290 $[M]^+$ (8), 272 (26), 257 (19), 137 (100), 95 (80); HREIMS *m*/*z* 290.2246 (calcd for $C_{19}H_{30}O_2$, 290.2246).

Compound 3: colorless oil; $[\alpha]^{25}_D$ +21.4 (*c* 0.17, $CHCl_3$); IR(film) ν_{max} 3050, 2925, 1720, 1644, 1607, 1336, 890, 830 cm^{-1}; ^{1}H, ^{13}C NMR, see Table 1; EIMS *m*/*z* 300 $[M]^+$ (42), 285 (27), 162 (97), 137(26), 110 (88), 42 (100); HREIMS *m*/*z* 300.2097 (calcd for $C_{20}H_{28}O_2$, 300.2089).

Compound 4: colorless oil; $[\alpha]^{25}_D$ +11 (*c* 0.05, $CHCl_3$); IR (film) ν_{max} 3600−2400, 2926, 1697, 1649, 1420, 1282, 891 cm^{-1}; ^{1}H, ^{13}C NMR, see Table 1; EIMS *m*/*z* 262 $[M]^+$ (7), 247 (1), 177 (17), 137 (100); HREIMS *m*/*z* 262.1936 (calcd for $C_{17}H_{26}O_2$, 262.1933).

Compound 5: oil; $[\alpha]^{24}_D$ −1.3 (*c* 0.86, EtOH); ^{1}H NMR ($CDCl_3$, 500 MHz) *δ* 1.51 (1H, ddd, *J* = 14, 10, 10 Hz, H-4), 1.64 (1H, ddd, *J* = 14, 3, 3 Hz, H-4), 1.67 (2H, m, H-6), 1.70 (2H, m, H-2), 2.51 (1H, ddd, *J* = 14, 8, 8 Hz, H-7), 2.57 (1H, ddd, *J* = 14, 9, 7 Hz, H-1), 2.61 (1H, ddd, *J* = 14, 8, 8 Hz, H-7), 2.68 (1H, ddd, *J* = 14, 9, 6 Hz, H-1), 3.80 (2H, m, H-5), 3.80 (2H, m, H-3), 3.81 (3H, s, −OCH_3), 4.22 (1H, d, *J* = 3 Hz, −OH), 4.24 (1H, d, *J* = 3 Hz, −OH), 6.52 (1H, dd, *J* = 8, 2 Hz, H-6″), 6.64 (1H, dd, *J* = 8, 2 Hz, H-6′), 6.69 (1H, d, *J* = 2 Hz, H-2″), 6.70 (1H, d, *J* = 8 Hz, H-5″), 6.71 (1H, d, *J* = 8 Hz, H-5′), 6.81 (1H, d, *J* = 2 Hz, H-2′), 7.29 (1H, br s, phenol-OH), 7.66 (2H, br s, phenol-OH); ^{13}C NMR ($CDCl_3$, 125 MHz) *δ* 31.7 (C-7), 32.0 (C-1), 41.1 (C-2, 6), 44.3 (C-4), 56.1 (−OCH_3), 71.1 (C-5), 71.7 (C-3), 112.7 (C-2′), 115.5 (C-5″), 115.9 (C-5′), 116.2 (C-2″), 120.3 (C-6″), 121.4 (C-6′), 134.7 (C-1′), 135.0 (C-1″), 143.7 (C-4″), 145.3 (C-4′), 145.7 (C-3″), 148.1 (C-3′); EIMS *m*/*z* 362 $[M]^+$ (18), 344 (6), 137 (100), 123 (63); HREIMS *m*/*z* 362.1725 (calcd for $C_{20}H_{26}O_6$, 362.1729).

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Supporting Information Available: Table and figure of ^{1}H, ^{13}C NMR data and HMBC correlations for compound **1**. Figures of key HMBC and NOESY correlations for compounds **2** and **3**. Structures of known compounds isolated from *Z. ottensii*. This information is available free of charge via the Internet at http://pubs.acs.org.

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