Five New Sesquiterpenoids and a New Diterpenoid from *Erigeron annuus* (L.) Pers., *Erigeron philadelphicus* L. and *Erigeron sumatrensis* Retz.

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The aerial parts of *Erigeron annuus* (L.) Pers., *E. philadelphicus* L. and *E. sumatrensis* Retz. (Compositae) have been investigated chemically. A new sesquiterpenoid, 6*β*,14-epoxyeudesm-4(15)-en-1*β*-ol (1), and a new diterpenoid, philadelphinone (6), have been isolated from *E. philadelphicus*. Four new sesquiterpenoids, (7*R)-opposit-4(15)-ene-1*β*,7-diol (2), 11-methoxyopposit-4(15)-en-1*β*-ol (3), 15-methoxyisodauc-3-ene-1*β*,5*α*-diol (4) and 10*α*-hydroxycadin-4-en-15-al (5), have been isolated from *E. annuus*. Compounds 2 and 4 were also isolated from *E. sumatrensis*. The structures of the new compounds were elucidated on the basis of their spectral data.**

Key words *Erigeron annuus*; *Erigeron philadelphicus*; *Erigeron sumatrensis*; Compositae; sesquiterpenoid; diterpenoid

Genus *Erigeron* is a common group of Compositae plants, and *E. annuus* (L.) Pers. (himejyon in Japanese), *E. philadelphicus* L. (harujion in Japanese) and *E. sumatrensis* Retz. (oarechinogiku in Japanese) are now, as naturalized weeds, widely distributed throughout urban and rural areas of Japan.[1] Among these, *E. annuus* has been used as an hypoglycemic drug in China.[2] The constituents of *E. annuus*, *E. philadelphicus* and *E. sumatrensis* have been previously investigated and shown to contain monoterpenoids,[3,4] sesquiterpenoids,[3,4] diterpenoid,[5] phenolic compounds,[6] polyacetylenic compounds[7] and *γ*-pyrone derivatives.[1] Recently we reported the isolation and structural elucidation of sterols and triterpenoids from the aerial parts and roots of these three plants.[8] As a part of our continuing study of the constituents of the genus *Erigeron* plants, we now report the isolation and structural elucidation of five new sesquiterpenoids, 6*β*,14-epoxyeudesm-4(15)-en-1*β*-ol (**1**), (7*R**)-opposit-4(15)-ene-1*β*,7-diol (**2**), 11-methoxyopposit-4(15)-en-1*β*-ol (**3**), 15-methoxyisodauc-3-ene-1*β*,5*α*-diol (**4**) and 10*α*-hydroxycadin-4-en-15-al (**5**), and a new diterpenoid, philadelphinone (**6**), as well as nine known compounds, oppsit-4(15)-ene-1*β*,11-diol (**7**),[9] eudesm-4(15)-ene-1*β*,6*α*-diol (**8**),[10] 6*α*-methoxyeudesm-4(15)-en-1*β*-ol (**9**),[9] eudesm-4(15)-ene-1*β*,5*α*-diol (**10**),[10] 4*α*,15-epoxyeudesmane-1*β*,6*α*-diol (**11**),[10] 1*α*-hydroxyisodauc-4-en-15-al (**12**),[11] aromadendrane-4*β*,10*β*-diol (**13**),[12] (5*E*)-germacra-5,10(14)-dien-1*β*,4*β*-diol (**14**)[13] and erigerol (**15**)[5] from the aerial parts of *E. annuus* (compounds **2**—**5**, **7**—**12**), *E. philadelphicus* (compounds **1**, **6**, **8**, **15**) and *E. sumatrensis* Retz. (compounds **2**, **4**, **7**—**9**, **11**—**14**). This is the first isolation of compounds **7**—**14** from these plants. Extraction and isolation were carried out as described in the Experimental section.

Compound **1** was isolated as a colorless amorphous solid, $[\alpha]_D$ +14.6°. The molecular formula was determined to be $C_{15}H_{24}O_2$ by high-resolution (HR)-electron ionization (EI)-MS, indicating four degrees of unsaturation. The IR spectrum showed the presence of a hydroxyl group (3429 cm^{-1}). The ^{1}H- (Table 1) and ^{13}C-NMR spectra (Table 2), obtained

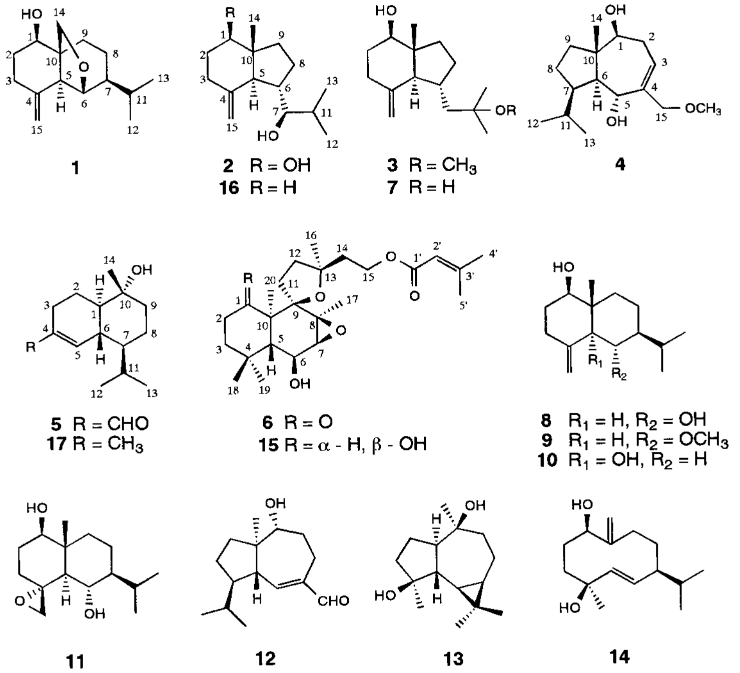

Chart 1

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Table 1. ^{1}H-NMR Chemical Shifts of Compounds **1**—**6** (600 MHz, $CDCl_3$)[a]

Proton	**1**	**2**	**3**	**4**[b]	**5**	**6**[b]
1	3.84 (1H, dd, 11.4, 5.5)	3.59 (1H, dd, 11.4, 4.8)	3.53 (1H, dd, 11.7, 4.4)	3.57 (1H, m)	1.35 (1H, ddd, 10.6, 10.6, 1.8)	
2	α 1.96 (1H, dddd, 12.5, 5.5, 3.7, 3.3) β 1.60 (1H, m)	α 1.87 (1H, m) β 1.50 (1H, dddd, 13.2, 13.2, 11.4, 5.1)	α 1.80 (1H, m) β 1.50 (1H, m)	α 2.58 (1H, m) β 2.24 (1H, m)	α 2.18 (1H, m) β 1.22 (1H, m)	α 2.16 (1H, m) β 2.77 (1H, ddd, 15.1, 12.2, 4.4)
3	α 2.06 (1H, ddd, 13.9, 13.2, 3.7) β 2.39 (1H, ddd, 13.2, 3.7, 3.3)	α 2.12 (1H, ddd, 13.6, 13.2, 5.5) β 2.30 (1H, m)	α 2.02 (1H, m) β 2.29 (1H, ddd, 13.6, 5.1, 1.8)	5.89 (1H, ddd, 6.8, 2.4, 2.4)	α 2.08 (1H, m) β 2.48 (1H, m)	α 1.36 (1H, m) β 1.76 (1H, ddd, 14.1, 4.4, 4.4)
5	1.99 (1H, br s)	1.84 (1H, d, 10.6)	1.52 (1H, d, 10.6)	4.39 (1H, br d, 9.8)	6.86 (1H, br s)	2.38 (1H, d, 11.0)
6	4.57 (1H, s)	2.33 (1H, m)	2.13 (1H, m)	2.44 (1H, dd, 11.0, 9.8)	2.02 (1H, m)	4.05 (1H, ddd, 11.2, 11.0, 2.7)
7	1.07 (1H, ddd, 13.6, 8.4, 5.1)	3.23 (1H, br d, 9.9)	a 1.27 (1H, dd, 13.9, 10.3) b 1.84 (1H, d, 13.9)	2.58 (1H, m)	1.22 (1H, m)	3.21 (1H, d, 2.7)
8	α 1.46 (1H, m) β 1.77 (1H, m)	α 1.33 (1H, m) β 1.91 (1H, m)	2.07 (2H, m)	a 1.59 (1H, m) b 1.66 (1H, m)	α 1.71 (1H, m) β 1.22 (1H, m)	
9	α 1.35 (1H, dddd, 12.8, 12.5, 5.1, 1.8) β 2.17 (1H, br dd, 12.5, 4.8)	α 1.39 (1H, m) β 1.76 (1H, m)	α 1.41 (1H, m) β 1.71 (1H, m)	a 1.55 (1H, m) b 1.69 (1H, m)	α 1.46 (1H, m) β 1.86 (1H, m)	
11	1.60 (1H, m)	1.76 (1H, m)		2.37 (1H, m)	2.24 (1H, m)	a 1.86 (1H, m) b 3.05 (1H, ddd, 17.1, 14.4, 9.8)
12	0.89 (3H, d, 6.6)	0.91 (3H, d, 7.0)	1.17 (3H, s)[c]	0.90 (3H, d, 6.8)	0.86 (3H, d, 7.0)	a 1.86 (1H, m) b 1.94 (1H, ddd, 13.9, 9.8, 2.7)
13	0.96 (3H, d, 6.6)	1.00 (3H, d, 7.0)	1.18 (3H, s)[c]	0.92 (3H, d, 7.1)	0.99 (3H, d, 7.0)	
14	a 3.61 (1H, d, 8.1) b 3.82 (1H, dd, 8.1, 1.8)	0.67 (3H, s)	0.64 (3H, s)	0.82 (3H, s)	1.15 (3H, s)	1.70 (2H, m)
15	4.89 (2H, d, 1.8)	a 4.81 (1H, d, 1.5) b 4.95 (1H, d, 1.5)	a 4.61 (1H, d, 1.5) b 4.85 (1H, d, 1.5)	a 3.82 (1H, d, 9.0) b 4.09 (1H, dd, 9.0, 1.0)	9.45 (1H, s)	4.09 (2H, m)
16						1.36 (3H, s)
17						1.47 (3H, s)
18						1.28 (3H, s)
19						1.12 (3H, s)
20						1.03 (3H, s)
2′						5.64 (1H, qq, 1.2, 1.2)
4′						1.89 (3H, d, 1.2)
5′						2.16 (3H, d, 1.2)
OCH_3			3.19 (3H, s)	3.44 (3H, s)		

a) Coupling constants (*J* in Hz) are given in parentheses. *b*) Measured at 400 MHz. *c*) Assignments are interchangeable.

with the aid of a ^{1}H-detected heteronuclear multiple quantum coherence (HMQC) and distorsionless enhancement by polarization transfer (DEPT) spectra, showed signals due to two secondary methyl groups [δ_H 0.89 (3H, H_3-12), 0.96 (3H, H_3-13); δ_C 20.3 (C-12), 20.9 (C-13)], an oxygenated methylene [δ_H 3.61 (1H, H_a-14), 3.82 (1H, H_b-14); δ_C 69.8 (C-14)], two oxygenated methines [δ_H 3.84 (1H, H-1), 4.57 (1H, H-6); δ_C 74.2 (C-1), 77.6 (C-6)] and an exomethylene [δ_H 4.89 (2H, H_2-15); δ_C 107.4 (C-15), 144.0 (C-4)]. The ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY) spectrum of **1** indicated connectivities of C-1 to C-3, C-7 to C-9, C-7 to C-11, and C-11 to C-12 and C-13 (Fig. 1). Interpretation of the ^{1}H-detected heteronuclear multiple bond connectivity (HMBC) spectrum revealed correlations from H-6 to C-4 and C-8; H_a-14 to C-5, C-6 and C-9; H_b-14 to C-1 and C-9; and H_2-15 to C-3 and C-5 (Fig. 1). Therefore, the planar structure of **1** was deduced to be 6,14-epoxyeudesm-4(15)-en-1-ol. The relative stereochemistry was determined as follows. A W-type coupling between H_α-9 and H_b-14 (J=1.8 Hz) indicated their anticoplanar orientation (Fig. 2). The nuclear Overhauser effect correlation spectroscopy (NOESY) cross peaks observed between H_β-2 and H_b-14, H-5 and H-7, and H_β-9 and H_a-14 implied a *trans*-junction for the A/B rings, and that the isopropyl group at C-7 had β configuration (Fig. 2). The coupling constants for H-1 (dd, J=11.4, 5.5 Hz) suggested that the hydroxyl group at C-1 had β configuration. On the basis of the above data, the structure of **1** was determined to be 6β,14-epoxyeudesm-4(15)-en-1β-ol. Compound **1** is the first example of a naturally occurring eudesmane-type sesquiterpenoid with an ether linkage between C-6 and C-14.

Compound **2** was isolated as a colorless amorphous solid, $[\alpha]_D$ +36.8°. The molecular formula was determined to be $C_{15}H_{26}O_2$ by HR-EI-MS. The IR spectrum showed the presence of a hydroxyl group (3599, 3445 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra of **2** were similar to those of **16**,[14] except for the presence of one more hydroxyl group. The position of this hydroxyl group was determined to be attached at C-1 by the HMBC spectrum, in which a cross peak was observed between H_3-14 at δ 0.67 and C-1 at δ 79.0. The coupling constants for H-1 (dd, J=11.4, 4.8 Hz) suggested that the hy-

Table 2. ^{13}C-NMR Chemical Shifts of Compounds **1**—**6** (150 MHz, $CDCl_3$)

Carbon	1	2	3	4$^{a)}$	5	6$^{a)}$
1	74.2	79.0	79.4	78.6	49.7	216.5
2	32.7	31.9	31.9	35.3	21.37	39.1$^{c)}$
3	33.6	34.9	34.7	133.3	22.2	39.2$^{c)}$
4	144.0	148.9	145.9	135.1	141.8	32.2
5	54.0	56.4	58.0	84.3	151.6	43.4
6	77.6	39.4	32.5	49.0	41.4	68.7
7	49.1	82.7	45.9	46.4	45.6	65.8
8	23.5	26.0	30.4	21.8	22.1	64.6
9	35.7	37.3	37.4	39.0	41.9	88.2
10	49.6	49.6	47.6	46.1	72.1	54.3
11	30.4	31.4	75.1	26.2	26.2	29.2
12	20.3	14.7	25.5$^{b)}$	19.2	15.2	38.6
13	20.9	20.6	25.5$^{b)}$	24.1	21.39	83.1
14	69.8	12.3	12.0	12.8	20.6	40.0
15	107.4	107.7	106.6	79.9	194.5	60.7
16						27.6
17						22.7
18						33.9
19						26.4
20						17.0
1′						166.6
2′						116.0
3′						156.6
4′						27.4
5′						20.2
OCH_3			49.2	58.3		

a) Measured at 100 MHz. *b*) Signals overlapped. *c*) Assignments are interchangeable.

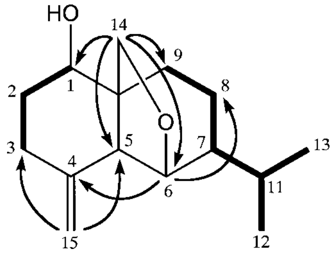

Fig. 1. ^{1}H–^{1}H COSY (Bold Lines) and HMBC (Full-Line Arrows) Correlations for **1**

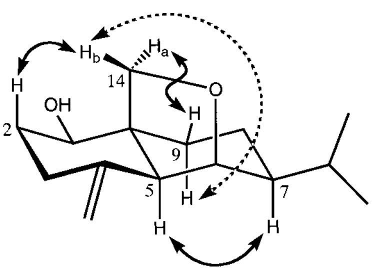

Fig. 2. NOEs (Full-Line Arrows) and W-Type Coupling (Dotted-Line Arrows) in **1**

droxyl group at C-1 had β configuration, which was supported by the NOESY cross peak between H_α-1 and H-5. The relative stereochemistry at C-7 was determined to be *R** by comparison of ^{1}H- and ^{13}C-NMR data with those of **16**.[14] From the above data, the structure of **2** was determined to be (7*R**)-opposit-4(15)-ene-1β,7-diol.

Compound **3** was isolated as a colorless amorphous solid, $[\alpha]_D$ +48.8°, and the molecular formula was determined to

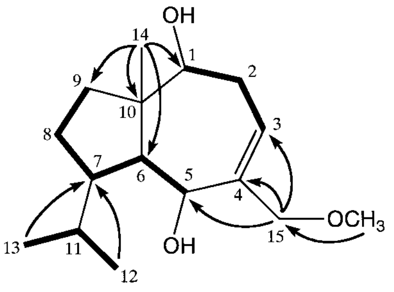

Fig. 3. ^{1}H–^{1}H COSY (Bold Lines) and HMBC (Full-Line Arrows) Correlations for **4**

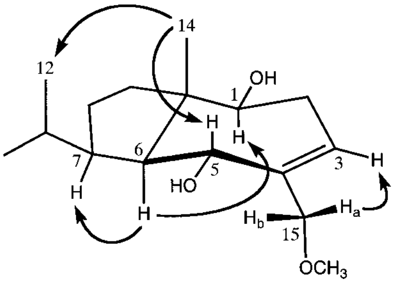

Fig. 4. NOEs Detected for **4**

be $C_{16}H_{28}O_2$ by HR-EI-MS. The IR spectrum showed the presence of a hydroxyl group (3600 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra of **3** were virtually identical to those of **7**, except for the presence of a methoxyl group (δ_H 3.19; δ_C 49.2) in place of a hydroxyl group at C-11. The C-11 position of this methoxyl group was confirmed by HMBC spectrum, in which a cross peak was observed between the methoxyl group at δ 3.19 and C-11 at δ 75.1. Based on the above evidence, the structure of **3** was determined to be 11-methoxy-opposit-4(15)-en-1β-ol. Compounds **2** and **3** are the first oppositane-type sesquiterpenoids isolated from the genus *Erigeron* plants.

Compound **4** was isolated as a colorless amorphous solid, $[\alpha]_D$ −57.2°. The molecular formula was determined to be $C_{16}H_{28}O_3$ by negative ion HR-FAB-MS. The IR spectrum showed the presence of a hydroxyl group (3608, 3280 cm^{-1}), while the ^{1}H- and ^{13}C-NMR spectra showed signals due to a tertiary methyl group [δ_H 0.82 (3H, H_3-14); δ_C 12.8 (C-14)], two secondary methyl groups [δ_H 0.90 (3H, H_3-12), 0.92 (3H, H_3-13); δ_C 19.2 (C-12), 24.1 (C-13)], a methoxyl group (δ_H 3.44; δ_C 58.3), an oxygenated methylene [δ_H 3.82 (1H, H_a-15), 4.09 (1H, H_b-15); δ_C 79.9 (C-15)], two oxygenated methines [δ_H 3.57 (1H, H-1), 4.39 (1H, H-5); δ_C 78.6 (C-1), 84.3 (C-5)] and a trisubstituted double bond [δ_H 5.89 (1H, H-3); δ_C 133.3 (C-3), 135.1 (C-4)]. The ^{1}H–^{1}H COSY spectrum indicated connectivities of C-1 to C-3, C-5 to C-9, and C-11 to C-12 and C-13 (Fig. 3). Interpretation of the HMBC spectrum revealed correlations from H_3-12 and H_3-13 to C-7; H_3-14 to C-1, C-6, C-9 and C-10; H_2-15 to C-3, C-4 and C-5; and a methoxyl group to C-15 (Fig. 3). Therefore, the planar structure of **4** was deduced to be 15-methoxyisodauc-3-ene-1,5-diol. Next, a series of difference nuclear Overhauser effect (NOE) experiments were carried out on **4** in order to determine the relative stereochemistry of the molecule. As shown in Fig. 4, irradiation at δ 0.90 (H_3-14) caused NOE enhancement in the signals of H-5 and H_3-12, and irradiation

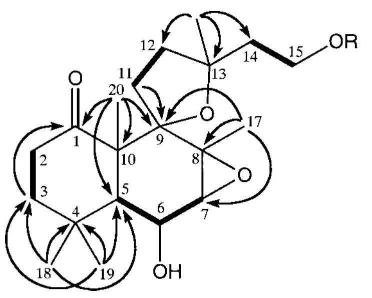

Fig. 5. ^{1}H–^{1}H COSY (Bold Lines) and HMBC (Full-Line Arrows) Correlations for **6**

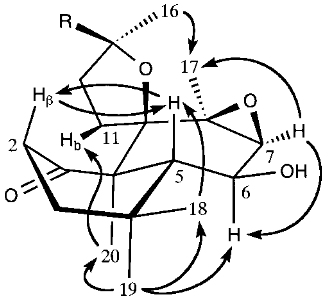

Fig. 6. NOEs Detected for **6**

at δ 2.44 (H-6) caused NOE enhancement in the signals of the H-1 and H-7. These NOEs implied a *trans*-junction for the A/B rings, and that the configuration at the C-1 and C-5 hydroxyl and C-7 isopropyl groups should be β, α and β, respectively. The geometry of the trisubstituted double bond at C-3 was shown to be *Z*. Accordingly, irradiation at δ 3.82 (H$_a$-15) caused NOE enhancement in the signals of the H-3. On the basis of this data, the structure of **4** was determined to be 15-methoxyisodauc-3-ene-1β,5α-diol. Compound **4** is the first isodaucane-type sesquiterpenoid isolated from the genus *Erigeron* plants.

Compound **5** was isolated as a colorless amorphous solid, $[\alpha]_D$ $-12.8°$. The molecular formula was determined to be $C_{15}H_{24}O_2$ by HR-EI-MS. The IR spectrum showed the presence of a hydroxyl group (3600, 3447 cm^{-1}) and an unsaturated aldehyde group (1682, 1638 cm^{-1}). UV spectrum also suggested the presence of an unsaturated aldehyde group (λ_{max}: 228 nm). The ^{1}H- and ^{13}C-NMR spectra of **5** were closely related to those of **17**[15] except that the olefinic methyl group at C-4 of **17** was replaced by an aldehyde group [δ_H 9.45 (1H, H-15); δ_C 194.5 (C-15)] in **5**. The C-4 position of an aldehyde group was confirmed by the HMBC spectrum, in which a cross peak was observed between H-15 at δ 9.45 and C-4 at δ 141.8. From this data, the structure of **5** was determined to be 10α-hydroxycadin-4-en-15-al. Misra *et al.*[16] suggested that compound **5** was a possible biogenetic precursor to the isodaucane-type sesquiterpenoids. Compound **5** has been synthesized by Kuo *et al.*,[17] but its isolation from natural sources has not so far been reported.

Compound **6**, termed philadelphinone, was isolated as a colorless amorphous solid, $[\alpha]_D$ $-73.8°$. The molecular formula was determined to be $C_{25}H_{38}O_6$ by HR-EI-MS. The IR spectrum showed the presence of a hydroxyl group (3570 cm^{-1}), a six-membered ring ketone (1704 cm^{-1}) and an α,β-unsaturated ester (1704, 1652 cm^{-1}). The ^{1}H- and ^{13}C-NMR spectra of **6** were similar to those of **15**, except that the C-1 hydroxyl group in **15** was replaced by a carbonyl group in **6**. The ^{1}H–^{1}H COSY and HMBC correlations as shown in Fig. 5 confirmed this planar structure. The relative stereochemistry of **6** was deduced to be the same as **15** by difference NOE experiments (Fig. 6). The coupling constants for H$_\beta$-2 (ddd, J=15.1, 12.2, 4.4 Hz) and the NOE between H$_\beta$-2 and H-5, led us to establish that the ring A is in a boat conformation, due to the presence of steric effects between the carbonyl group at C-1 with the oxygen atom at C-9. Noteworthy is the fact that the chemical shifts of methylene protons [δ_H 1.86 (1H, H$_a$-11), 3.05 (1H, H$_b$-11)] at C-11 are considerably different from each other due to an anisotropic effect of the carbonyl group at C-1. Thus, the structure of **6** was determined to be as shown in Chart 1.

Experimental

General Procedures Optical rotations were determined using a JASCO DIP-360 digital polarimeter. IR spectra were recorded with a Perkin-Elmer FT-IR 1725X spectrophotometer and UV spectra on a Beckman DU-64 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded using a JEOL JNM-LA 600 (600 and 150 MHz, respectively) and JEOL JNM-LA 400 (400 and 100 MHz, respectively) spectrometers. Chemical shifts are given on a δ (ppm) scale, with tetramethylsilane as an internal standard. The HR-EI-MS and HR-FAB-MS were recorded on a JEOL JMS-DX 303 mass spectrometer. Column chromatography was carried out on Kieselgel 60 (Merck; 230—400 mesh) and Cosmosil 75C$_{18}$-OPN (Nacalai Tesque). Preparative HPLC was carried out on a Tosoh HPLC system (pump, CCPM; detector, RI-8020 and UV-8020); Condition A, Column, TSKgel ODS-120T, 7.8 mm i.d.×30 cm (Tosoh); mobile phase, MeOH–H$_2$O (1 : 1); column temperature, 40 °C; flow rate, 1.5 ml/min; RI detector; Condition B, Column, Cosmosil 5SL, 10 mm i.d.×25 cm (Nacalai Tesque); mobile phase, *n*-hexane–acetone (9 : 1); flow rate, 1.0 ml/min; UV detector, 235 nm; Condition C, Column, TSKgel ODS-120T, 7.8 mm i.d.×30 cm (Tosoh); mobile phase, MeOH; column temperature, 40 °C; flow rate, 1.5 ml/min; RI detector.

Plant Material The aerial parts of *Erigeron annuus* were collected in Sendai City in Miyagi Prefecture, Japan, in July of 2001, those of *Erigeron philadelphicus* in Sendai City in April, 2002, and those of *Erigeron sumatrensis* in Sendai City in October, 2000.

Extraction and Isolation *E. annuus*: The aerial parts of *E. annuus* (5.3 kg) were extracted with MeOH at room temperature for 2 weeks. The MeOH extract was concentrated under reduced pressure and the residue was suspended in a small excess of water. This suspension was extracted with CHCl$_3$, Et$_2$O, AcOEt and *n*-BuOH, successively. The CHCl$_3$-soluble fraction was concentrated under reduced pressure to afford a residue (79.4 g). A part of this residue (67.0 g) was chromatographed on a silica-gel column using *n*-hexane–AcOEt (7 : 1—1 : 7) and CHCl$_3$–MeOH (9 : 1—1 : 1) to afford 62 fractions (frs. 1—62) . Fraction 9 was purified by preparative HPLC (Condition A) to give **3** (0.4 mg), **9** (0.3 mg) and **12** (1.1 mg). Fraction 10 was purified by preparative HPLC (Condition A) to give **4** (3.0 mg). Fraction 11 was purified by preparative HPLC (Condition B) to give **5** (0.8 mg). Fraction 12 was purified by preparative HPLC (Condition A) to give **2** (2.7 mg), **8** (1.1 mg), **10** (1.7 mg) and **11** (0.7 mg). Fraction 19 was purified by preparative HPLC (Condition A) to give **7** (0.3 mg).

E. philadelphicus: The aerial parts of *E. philadelphicus* (2.5 kg) were extracted with MeOH at room temperature for 2 weeks. The MeOH extract was concentrated under reduced pressure and the residue was suspended in a small excess of water. This suspension was extracted with CHCl$_3$, Et$_2$O, AcOEt and *n*-BuOH, successively. The CHCl$_3$-soluble fraction was concentrated under reduced pressure to afford a residue (24.0 g), which was then chromatographed on a silica-gel column using *n*-hexane–AcOEt (7 : 1—1 : 7) and CHCl$_3$–MeOH (9 : 1—1 : 1) to afford 47 fractions (frs. 1—47) . Fraction 11 was purified by preparative HPLC (Condition A) to give **1** (1.4 mg) and **8** (0.8 mg). Fraction 16 was purified by Cosmosil 75C$_{18}$-OPN column chromatography [MeOH–H$_2$O (3 : 1)] to give **6** (1.5 mg), and Fraction 18 was purified by Cosmosil 75C$_{18}$-OPN column chromatography [MeOH–H$_2$O (3 : 1)] to give **15** (44.5 mg).

E. sumatrensis: The aerial parts of *E. sumatrensis* (4.0 kg) were extracted with MeOH at room temperature for 2 weeks. The MeOH extract was concentrated under reduced pressure and the residue was suspended in a small excess of water. This suspension was then successively extracted with

$CHCl_3$, Et_2O, AcOEt and *n*-BuOH. The $CHCl_3$-soluble fraction was concentrated under reduced pressure to afford a residue (80.7 g). A part of this residue (50.0 g) was chromatographed on a silica-gel column using *n*-hexane–AcOEt (7 : 1—1 : 7) and $CHCl_3$–MeOH (9 : 1—1 : 1) to afford 60 fractions (frs. 1—60) . Fraction 8 was purified by preparative HPLC (Condition A) to give **9** (0.7 mg), and Fraction 9 in the same way to give **4** (0.6 mg) and **12** (0.1 mg). Fraction 13 was purified by preparative HPLC (Condition C) to give **8** (0.4 mg) and **11** (0.3 mg). Fraction 15 was purified by preparative HPLC (Condition A) to give **2** (0.6 mg), and Fraction 23 by the same means to give **13** (0.6 mg) and **14** (0.3 mg).

All known compounds (**7**—**15**) were identified by comparison of their physical data with reported values.

6*β*,14-Epoxyeudesm-4(15)-en-1*β*-ol (**1**): Colorless amorphous solid. $[\alpha]_D^{26}$ +14.6° (c=0.1, $CHCl_3$). IR ν_{max} $CHCl_3$ cm^{-1}: 3429. HR-EI-MS *m/z*: 236.1748 (M^+, Calcd for $C_{15}H_{24}O_2$: 236.1776). ^1H-NMR (600 MHz, $CDCl_3$): see Table 1. ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 2.

(7*R**)-Opposit-4(15)-ene-1*β*,7-diol (**2**): Colorless amorphous solid. $[\alpha]_D^{26}$ +36.8° (c=0.3, $CHCl_3$). IR ν_{max} $CHCl_3$ cm^{-1}: 3599, 3445. HR-EI-MS *m/z*: 238.1951 (M^+, Calcd for $C_{15}H_{26}O_2$: 238.1933). ^1H-NMR (600 MHz, $CDCl_3$): see Table 1. ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 2.

11-Methoxyopposit-4(15)-en-1*β*-ol (**3**): Colorless amorphous solid. $[\alpha]_D^{26}$ +48.8° (c=0.04, $CHCl_3$). IR ν_{max} $CHCl_3$ cm^{-1}: 3600. HR-EI-MS *m/z*: 252.2099 (M^+, Calcd for $C_{16}H_{28}O_2$: 252.2089). ^1H-NMR (600 MHz, $CDCl_3$): see Table 1. ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 2.

15-Methoxyisodauc-3-ene-1*β*,5*α*-diol (**4**): Colorless amorphous solid. $[\alpha]_D^{27}$ −57.2° (c=0.3, $CHCl_3$). IR ν_{max} $CHCl_3$ cm^{-1}: 3608, 3280. HR-FAB-MS (negative ion mode; matrix, triethanolamine) *m/z*: 267.1920 ($[M-H]^-$, Calcd for $C_{16}H_{27}O_3$: 267.1960). ^1H-NMR (400 MHz, $CDCl_3$): see Table 1. ^{13}C-NMR (100 MHz, $CDCl_3$): see Table 2.

10*α*-Hydroxycadin-4-en-15-al (**5**): Colorless amorphous solid. $[\alpha]_D^{26}$ −12.8° (c=0.08, $CHCl_3$). IR ν_{max} $CHCl_3$ cm^{-1}: 3600, 3447, 1682, 1638. UV λ_{max} MeOH nm (log ε): 228 (3.7). HR-EI-MS *m/z*: 236.1788 (M^+, Calcd for $C_{15}H_{24}O_2$: 236.1776). ^1H-NMR (600 MHz, $CDCl_3$): see Table 1. ^{13}C-NMR (150 MHz, $CDCl_3$): see Table 2.

Philadelphinone (**6**): Colorless amorphous solid. $[\alpha]_D^{24}$ −73.8° (c=0.2, $CHCl_3$). IR ν_{max} $CHCl_3$ cm^{-1}: 3570, 1704, 1652. UV λ_{max} MeOH nm (log ε): 222 (4.1). HR-EI-MS *m/z*: 434.2688 (M^+, Calcd for $C_{25}H_{38}O_6$: 434.2668). ^1H-NMR (400 MHz, $CDCl_3$): see Table 1. ^{13}C-NMR (100 MHz, $CDCl_3$): see Table 2.

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